Researchers unveil complex defect structure of Li-ion cathode material

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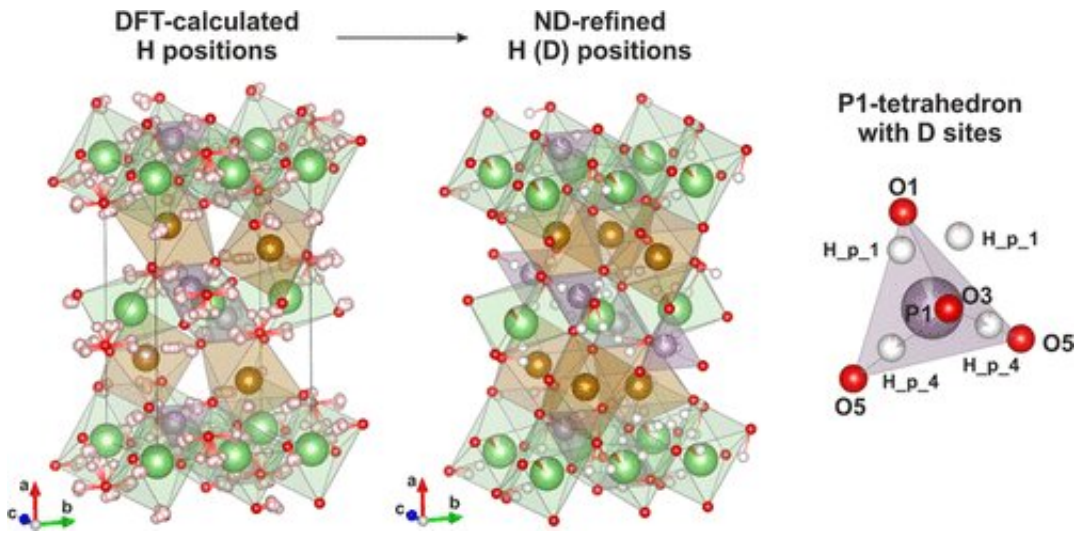

Graphical abstract. Credit: *Inorganic Chemistry* (2021). DOI: 10.1021/acs.inorgchem.0c03241

Skoltech scientists have studied the hydroxyl defects in $LiFePO_4$, a widely used cathode material in commercial lithium-ion batteries, contributing to the overall understanding of the chemistry of this material. This work will help improve the $LiFePO_4$ manufacturing process to avoid formation of adverse intrinsic structural defects which deteriorate its performance. The paper was published in the journal *Inorganic Chemistry*.

Lithium iron phosphate, $LiFePO_4$, is a safe, stable and affordable

cathode material for Li-ion batteries that has been very well optimized for practical applications despite its low conductivity and medium energy density. Yet scientists continue to study the various properties of this material, and in particular the impact of its defects on electrochemical performance.

"It is well known that $LiFePO_4$ materials usually have a considerable amount of Li/Fe antisite defects. This is a type of point defect when Li and Fe atoms exchange their positions in the crystal lattice. However, before us, nobody had assumed that the PO_4 part can be also defect-active in this material. We discovered that in some cases the PO_4 anion can be substituted by four or five OH groups, which has a negative effect on electrochemical performance of $LiFePO_4$-based batteries. Such defects are called OH defects or more specifically hydrogarnet-type hydroxyl defects," Dmitry Aksyonov, Skoltech Senior Research Scientist and the first author of the paper, explains.

Aksyonov, Assistant Professor Stanislav Fedotov, and Professor Artem Abakumov (CEST), with their colleagues, used a joint computational and experimental approach combining density functional theory and neutron diffraction to study the hydroxyl (OH) defects in $LiFePO_4$. They were also able to confirm their results experimentally in a $LiFePO_4$ sample.

"The hydrogarnet OH defects are well known in geology, but not so much in materials science. The presence of OH defects in $LiFePO_4$ could have been envisaged much earlier by drawing parallels with its structural analogs in the olivine mineral group. Therefore, the biggest takeaway from our work is probably that researchers should seek knowledge not only in their home field but in other fields as well," Aksyonov says.

Since OH defects are not trivial to detect, commercially produced

$LiFePO_4$ materials may have them as well, he notes, and it is important to have these deteriorating effects under control.

"The simplest practical outcome of this research would be to put efforts in modifying the synthesis procedure so as to fully eliminate this type of defects from the $LiFePO_4$ materials. However, our experience tells that fighting defects makes much less sense than turning them in our favor. So, the story has all chances to be continued," Stanislav Fedotov adds.

More information: Dmitry A. Aksyonov et al, Hydroxyl Defects in LiFePO4 Cathode Material: DFT+U and an Experimental Study, *Inorganic Chemistry* (2021). DOI: 10.1021/acs.inorgchem.0c03241

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