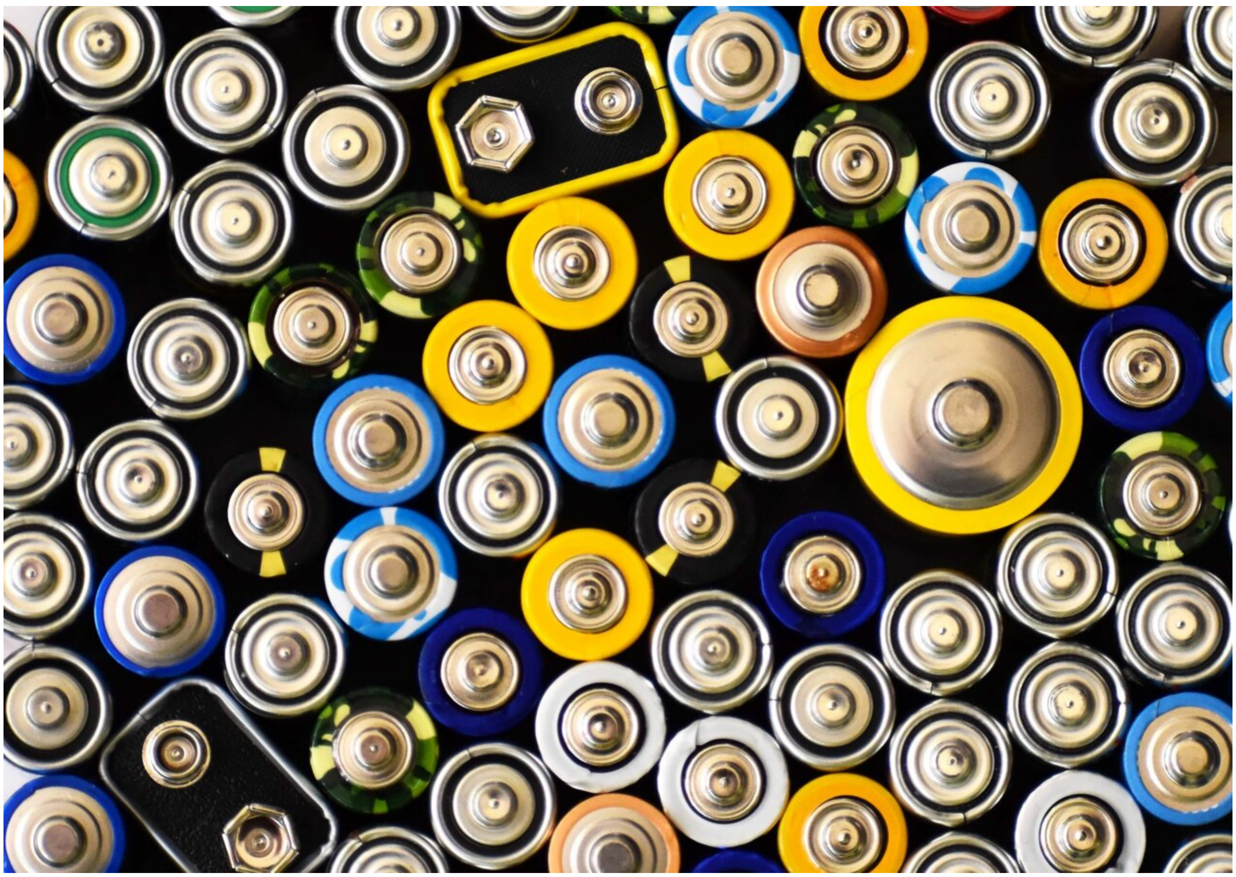
Cathode oxidation research overturns current thinking on batteries

July 19 2023



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Scientists have made a significant breakthrough in understanding and overcoming the challenges associated with Ni-rich cathode materials used in lithium-ion batteries. Researchers from the Universities of Birmingham, Cambridge, Warwick as well as The Faraday Institution, Didcot, published their findings (July 19) in *Joule*.

These materials have the potential to achieve both high voltages and capacities, but their practical applications have been hindered by structural instabilities and loss of oxygen.

Their study revealed that "oxygen hole" formation—where an oxygen ion loses an electron—plays a crucial role in the degradation of $LiNiO_2$ cathodes accelerating the release of oxygen which can then further degrade the cathode material.

Using a set of state-of-the-art computational techniques on UK regional supercomputers, the researchers examined the behavior of $LiNiO_2$ cathodes as they are charged. They found that during charging the oxygen in the material undergoes changes while the nickel charge remains essentially unchanged.

Co-author Prof Andrew J. Morris, from the University of Birmingham, said, "We found that the charge of the nickel ions remains around +2, regardless of whether it's in its charged or discharged form. At the same time the charge of the oxygen varies from -1.5 to about -1.

"This is unusual, the conventional model assumes that the oxygen remains at -2 throughout charging, but these changes show that the oxygen is not very stable, and we have found a pathway for it to leave the nickel-rich cathode."

The researchers compared their calculations with experimental data and found that their results aligned well with what was observed. They proposed a mechanism for how oxygen is lost during this process, involving the combination of oxygen radicals to form a peroxide ion, which is then converted into oxygen gas, leaving vacancies in the material. This process releases energy and forms singlet oxygen, a highly reactive form of oxygen.

"Potentially, by adding dopants that reduce oxygen redox, while promoting transition-metal redox particularly at the surface, mitigating the generation of singlet oxygen, we can enhance the stability and longevity of these type of lithium-ion batteries, paving the way for more efficient and reliable energy storage systems," first author Dr. Annalena Genreith-Schriever from the University of Cambridge adds.

Lithium-ion batteries are widely used for various applications because of their high energy density and rechargeability, but challenges associated with the stability of cathode materials have hindered their overall performance and lifespan.

More information: Andrew J. Morris, Oxygen Hole Formation Controls Stability in LiNiO2 Cathodes, *Joule* (2023). DOI: 10.1016/j.joule.2023.06.017.
www.cell.com/joule/fulltext/S2542-4351(23)00267-2

Provided by University of Birmingham