Study explores the viability of realizing stable high-voltage O-redox cathodes

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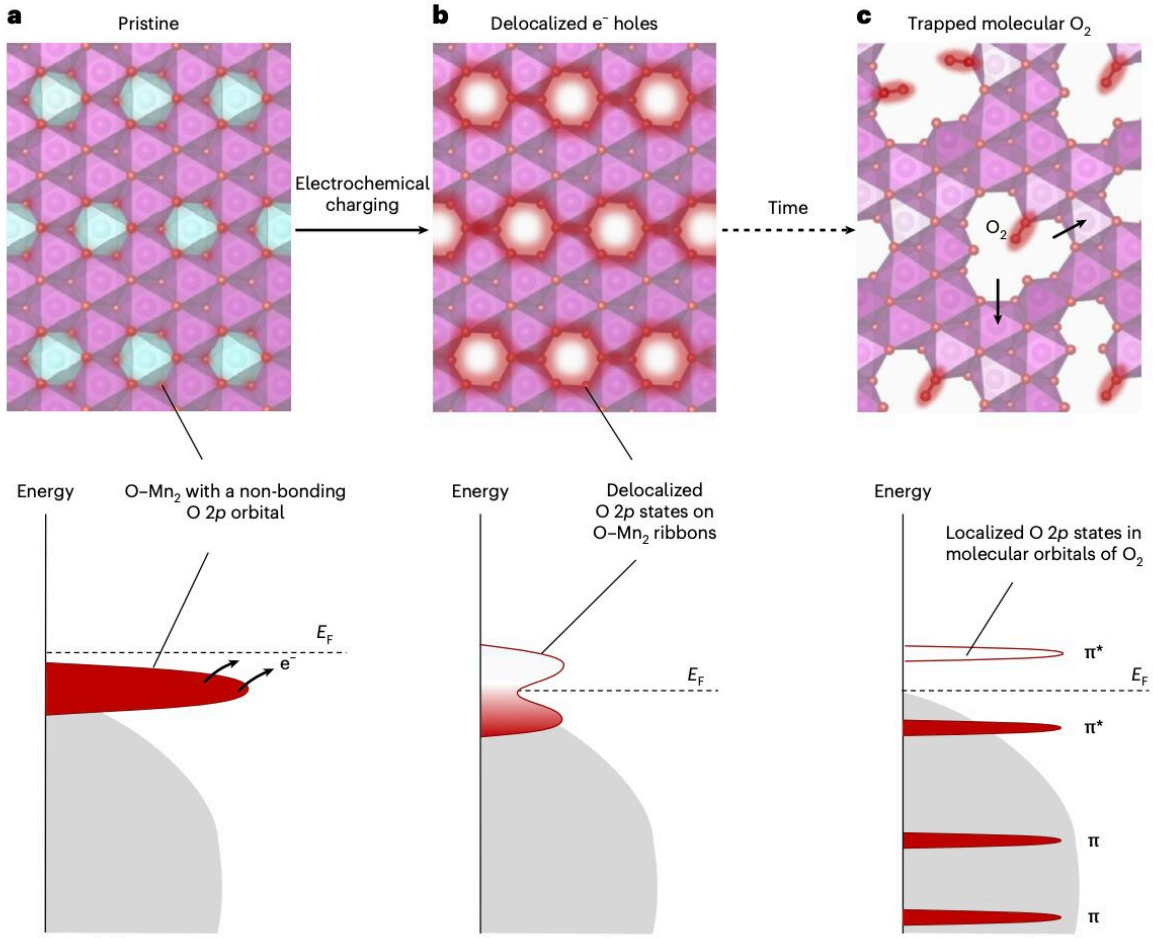

a–c, Structural schematics illustrating the pristine structure (a) the charged structure with delocalized electron holes on O–Mn2 (b) and a charged structure after condensation of the delocalized holes to form molecular O2 (c). Below each structure are schematic density of-states plots illustrating the changes to the

O 2p states near the Fermi level. Credit: *Nature Energy* (2023). DOI: 10.1038/s41560-023-01211-0.

To meet rising energy demands and power the countless electronic devices on the market, researchers will need to develop new advanced battery technologies. These technologies should ideally have higher energy densities and longer lifetimes, so that they can store more energy and last longer.

The energy densities of existing rechargeable lithium-ion (LiBs) and sodium-ion (NaBs) batteries have so far been difficult to increase. A key reason for this is that their cathodes, which are generally made of transition metal oxides and operate by removing and reinserting Li^+ when the batteries are being charged or discharged, can only compensate charge through oxidation and reduction of the transition metal ions. This poses a limit on the overall charge that can be stored in the batteries.

Researchers at University of Oxford, University of Bath and Diamond Light Source have recently carried out a study exploring the potential of so-called "O-redox" cathodes for increasing the energy density of LiBs and NaBs. Their paper, published in *Nature Energy*, provides the first direct evidence of the nature of delocalized electron holes forming on O^{2-} ions in O-redox cathodes, which could guide the future development of alternative cathodes.

"We were interested in understanding the mechanism of reversible charge storage on the oxide ions in battery cathodes," Robert A. House, one of the researchers who carried out the study, told Tech Xplore. "There are currently only a small handful of known materials which can undergo oxygen redox reversibly and the chemistry behind this process was not clear. Revealing the nature of this charge storage mechanism

could help unlock new high energy density cathode materials for the next generation of rechargeable batteries."

The formation of molecular oxygen caused by the oxidation of oxide ions in cathodes is known to reduce the cycling stability of battery technologies. As suggested by their name, O-redox cathodes would rely on the oxidation of oxygen ions to provide batteries with additional capacities at high voltages.

House and his colleagues set out to better understand the nature of electron-holes on oxide ions, as this could ultimately inform the realization of reversible O-redox cathodes.

To do this, they used a combination of advanced characterization techniques, including high-resolution resonant inelastic X-ray scattering (RIXS), O nuclear magnetic resonance (NMR) and superconducting quantum interference device (SQUID) magnetometry.

"We chose to employ analytical tools capable of directly probing the oxygen in an archetypal example of a reversible oxygen redox cathode," House said. "These techniques allowed us to determine the distribution of charge across the oxide ions after charging the battery and follow how it changed with time. The data revealed that the charge was spread evenly (or delocalized) across specific oxygen environments which form ribbons through the structure."

In their experiments, House and his colleagues used $Na_{0.6}[Li_{0.2}Mn_{0.8}]O_2$a cathode material in which the conversion of oxidized O^{2-} into O_2 occurs slowly. This allowed them to thoroughly capture the change of oxygen hole states in the cathode over time.

"If we are to realize the full potential of high voltage oxygen redox cathodes, we need to find materials that can provide a stable support for

electron holes on oxygen," House explained. "Having shown that this is in principle possible by delocalising the charge across ribbons of oxide ions in the structure, there is hope that it might be possible to engineer stable oxygen redox cathodes using the learnings from our study."

The recent work by this team of researchers contributes to ongoing efforts aimed at creating truly reversible O-redox cathodes that would enable greater energy densities in LiBs and NaBs. In the future, their results could pave the way for further studies into O-redox chemistry, potentially enabling the design of promising cathodes for next-generation batteries.

"We are now continuing to push deeper with our understanding of oxygen redox chemistry and to apply our knowledge to discover new high energy density cathode materials," House added.

More information: Robert A. House et al, Delocalized electron holes on oxygen in a battery cathode, *Nature Energy* (2023). DOI: 10.1038/s41560-023-01211-0.