Controlling oxygen may stop batteries from slowly fading

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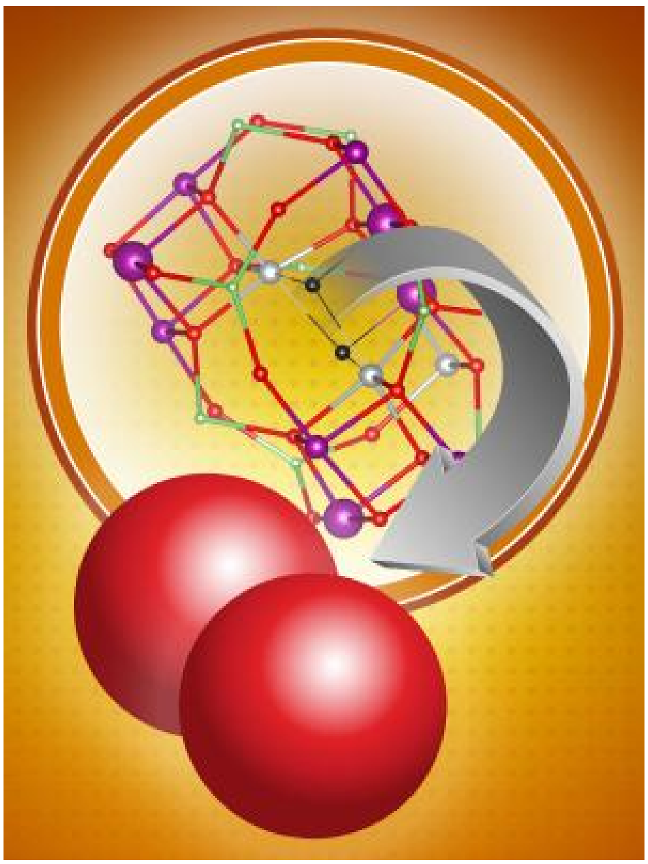

Next generation lithium-ion batteries fade, releasing less energy each time the battery is charged. Because the battery fades, it has to be replaced, at an environmental and financial cost. A recent study by theoreticians at Pacific Northwest National Laboratory and University College London answers decades-old questions about the underlying microscopic processes.

(Phys.org) —When oxygen atoms escape, they change the local electronic structure and cause the voltage to fade in a next-generation battery, according to theoreticians at Pacific Northwest National Laboratory and University College London, UK. A lithium, manganese, nickel cathode has a high energy density and charges and releases energy quickly, but it fades too soon for commercial use. The team found the release of oxygen leaves vacancies throughout the structure along with stray electrons. The vacancies promote structural disorder that reduces the energy barrier for lithium ions to leave the cathode and reduces the battery's voltage, just as seen in earlier experiments.

"Our simulated voltage curves respond like those seen in real experimental situation," said Dr. Maria Sushko, the materials scientist at PNNL who led the study. "We are modeling the material using a realistic structure with defects and disorder rather than some idealized material."

Lithium-ion batteries fade, releasing less energy each time the battery is charged. Over time, the battery's voltage declines to the point that it is no longer viable and has to be replaced, at both an environmental and financial cost. This study answers decades-old questions about the underlying microscopic processes. The team shows how the loss of oxygen atoms and the formation of nickel- and magnesium-rich areas cause fading. This new information assists in the knowledge-based design of longer lasting materials for cell phones, laptop computers, and electric cars.

"Overall, this research matters in moving forward on battery technologies," said Dr. Kevin Rosso, a Laboratory Fellow at PNNL who co-led this 6-month study. "Batteries that do not fade would let electronic devices work longer without recharging and make them more stable."

The researchers began with $LiNi_{0.5}Mn_{1.5}O_{4-?}$, shorthanded as LMNO, which could be a high-capacity material that quickly charges and discharges if it continually delivered the same voltage. Earlier experiments led the team to focus on the oxygen vacancies and the two electrons left when the oxygen leaves. Using quantum mechanical density functional theory, the team considered the possible configurations of the oxygen vacancies. They determined which arrangements matched the earlier experimental data. Then, they calculated the relative extraction rates of oxygen from different places in the lattice. With this information, they used PNNL Institutional Computing and other resources to accurately model the material.

They found that the presence neutral oxygen vacancies in the material favors disordered nickel arrangement in the lattice and the creation of nickel-rich and -poor areas. The vacancies resulting from oxygen atoms' departure leave behind two unpaired electrons, which get trapped on nearby manganese ions. In nickel-rich areas, the trapped electrons change the oxidation state of nearby manganese ions, from Mn+4 to Mn+3, producing shallow electron states that alter the stability of the material's lattice. These changes to the lattice lower the energy barrier to creating and healing lithium vacancies and lower the corresponding voltages.

In the end, the team determined that doping the cathode changes the local electronic structure to allow the battery to regularly take in and release the maximum voltage.

More information: Sushko, P. et al. 2013. Oxygen Vacancies and Ordering of d-Levels Control Voltage Suppression in Oxide Cathodes: the Case of Spinel $LiNi_{0.5}Mn_{1.5}O_{4-8}$, *Advanced Functional Materials.* DOI: 10.1002/adfm.201301205

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