

ENERGY SCIENCES

Reversible Lattice-Oxygen Reactions in Batteries



Chemical reactions involving manganese (Mn) and oxygen (O) in the crystal lattice of battery electrodes were quantified independently using an advanced spectroscopy technique. Color columns in the battery illustrations indicate the share of battery capacity from oxygen (red) and manganese (green) chemical reactions, from the first charge and discharge to the 100th cycle. (Credit: Berkeley Lab)

Oxygen reactions: plus or minus?

For a wide range of applications, from mobile phones to electric vehicles, the reversibility and cyclability of the chemical reactions occurring inside a rechargeable battery are key to commercial viability. Conventional wisdom had held that involving oxygen in a battery's electrochemical operation spontaneously triggers irreversible oxygen losses and parasitic surface reactions, reducing reversibility and safety. Recently however, the idea emerged that reactions involving lattice oxygen (i.e., oxygen that's part of the crystal-lattice structure vs oxygen on the surface) could be useful for improving battery capacity. Here, researchers report the first direct quantification of a strong, beneficial, and highly reversible chemical reaction involving lattice oxygen in electrodes made with low-cost elements.

Possibility of lattice-oxygen redox

Many rechargeable-battery electrodes are made of layers that combine oxygen with transition metals (TMs), a material class that includes relatively abundant elements such as iron, nickel, cobalt, and manganese. Oxidation-reduction (redox) reactions, which are central to battery capacity and operation, had previously been associated with these TM components. However, some TM-oxide materials demonstrated capacities far beyond what could be explained solely by TM redox, suggesting a possible contribution from the oxygen. Other studies indicated that a stable lattice-oxygen reaction would require rare and expensive TMs such as ruthenium or iridum. Although soft x-ray absorption spectroscopy helped spark these important developments, it is limited in its ability to differentiate between TM and oxygen signal contributions due to their mixed states (hybridization).

Scientific Achievement

Researchers used the Advanced Light Source (ALS) to quantify a strong, beneficial, and reversible (over hundreds of cycles) chemical reaction involving oxygen ions in the crystal lattice of battery electrode materials.

Significance and Impact

The results open up new ways to explore how to pack more energy into batteries with electrodes made out of low-cost, common materials.

Spectral maps distinguish oxygen states

In this study, researchers fabricated and tested a sodium-ion battery material $(Na_{2/3}Mg_{1/3}Mn_{2/3}O_2)$ in which manganese (Mn) is the TM. The sodium ions move in and out of the spaces between the TM-oxide layers during charging and discharging.

The samples were studied at ALS Beamline 8.0.1 using a specialized, ultrahigh-efficiency technique known as mRIXS (mapping of resonant inelastic x-ray scattering). This technique can distinguish between lattice-oxygen redox (the most useful oxygen activity) from mixed TMoxygen redox. With mRIXS, it's also possible to quantify reactions involving both anions (O) and cations (Mn) independently, allowing a precise understanding of the total battery capacity.



532



526 528 530 532 534 536 526 528 530 532 534 536 Excitation energy (eV)

Oxygen K-edge mRIXS maps of the $Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$ electrode, charged (top) and discharged (bottom), after 1 and 100 cycles. Red arrows indicate the lattice-oxygen redox feature.

Settling the reversibility debate

The results showed that a very strong lattice-oxygen redox reaction in $Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$ accounts for most of its capacity. Surprisingly, this strong reaction did not compromise reversibility: 87% of this capacity was retained after 100 charge-discharge cycles (directly seen in the mRIXS raw data). For comparison, the researchers also analyzed a more complex lithium-ion battery compound (Li_{1.17}Ni_{0.21}Co_{0.08}Mn_{0.54}O₂) that exhibits other types of oxygen activity. The researchers concluded that both sodium- and lithium-ion battery materials share the same fundamental mechanism of lattice-oxygen redox that can be highly reversible for hundreds of cycles.

The study settles the debate about the reversibility of lattice-oxygen redox in battery electrodes made of common elements. It also clarifies that reductions in reversibility can be attributed to non-lattice-oxygen activities, which were often mixed with lattice-oxygen redox reactions in previous studies.



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Future studies could focus on different electrode materials and designs, including the use of different surface coatings and

the introduction of doping agents to maximize beneficial lattice-oxygen reactions while suppressing others.

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