Energy boost confirmed in Li-rich disordered rock-salt oxyfluoride cathodes

For next-generation Li-ion batteries, researchers are developing higher capacity and higher energy density batteries with high energy density cathodes. For this, disordered rock-salt oxyfluorides have received significant attention due to their high capacity and lower voltage hysteresis. Li-ion cathodes bring an increment in capacity due to the invoking of redox chemistry on both the transition metal and oxide ions. To understand this phenomenon, M. Saiful Islam's group at the University of Bath analyzed an all-manganese oxyfluoride ($\text{Li}_{1.9}\text{Mn}_{0.95}\text{O}_{2.05}\text{F}_{0.95}$) using techniques including combined *operando* x-ray absorption spectroscopy,

high-resolution resonant inelastic x-ray scattering (RIXS), and *ab initio* modeling.

Ryan Sharpe, Islam, and colleagues from the University of Bath, the University of Oxford, the Diamond Light Source, and STFC ISIS Facility synthesized $\text{Li}_2\text{MnO}_2\text{F}$ and established that the compound possesses a cubic rock-salt structure, wherein each cation (Li^+ or Mn^{3+}) is octahedrally coordinated to six anions (O^{2-} or F^-) and vice versa. To confirm this structure, the environment of the Mn ions was studied using extended x-ray absorption fine structure measurements. The researchers also applied a neutron pair distribution function. Combining both techniques, they confirmed a disordered rock-salt structure. *Ab initio* simulations were also performed and confirmed that the disordered rock-salt structure does not exhibit the cooperative Jahn–Teller

distortion that is usually associated with manganese in an oxidation state of +3.

The analysis, reported in a recent issue of the *Journal of the American Chemical Society*. (<https://doi.org/10.1021/jacs.0c10270>), showed that molecular O_2 was formed inside the bulk, charged material, and was reversibly reduced to O^{2-} upon discharge. A combination of RIXS and *ab initio* simulations demonstrated that molecular O_2 is held within vacancy clusters in the structure. The trapped molecular O_2 also exhibits minimal mobility, making it more characteristic of a solid-like environment. “This rigid trapping of O_2 within close proximity to cation centers also helps to rationalize how it could be reduced to O^{2-} with ease on discharge,” the researchers write.

Evaluating the oxidation states, the research group demonstrated that the Mn redox process occurs between 3^+ and 4^+ with no evidence of other oxidation states. Further, as $\text{Li}_2\text{MnO}_2\text{F}$ already possesses an intrinsically disordered structure, it does not undergo the extensive structural rearrangements observed in layered honeycomb cathodes, which result in reduced voltage hysteresis on the first charge/discharge cycle. This work advances the understanding of fundamental redox mechanisms in Li-rich disordered rock salts. It also showcases the promise of these materials as more structurally stable oxygen-redox cathodes for higher capacities.

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Calculated structures of $\text{Li}_2\text{MnO}_2\text{F}$ (left) and $\text{Li}_{0.75}\text{MnO}_2\text{F}$ (middle), and the local environment of molecular O_2 in the bulk of $\text{Li}_{0.75}\text{MnO}_2\text{F}$ (right). Li, Mn, O, and F are indicated by green, purple, red, and gray, respectively. The weak Mn– O_2 and Li– O_2 interactions are indicated with dashed lines. Credit: *Journal of the American Chemical Society*.

CONGRATULATIONS!

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Journal of
MATERIALS RESEARCH

Published January 28, 2020 | JMR Volume 35, Issue 2