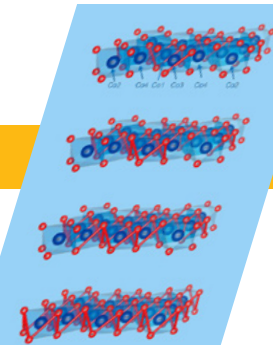
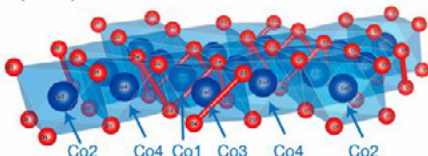
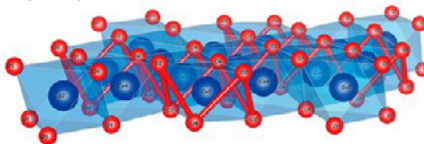
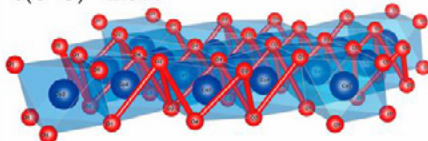
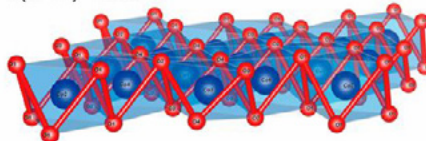


How a New Electrocatalyst Enables Ultrafast Reactions


 $d(\text{O}-\text{O}) < 2.4 \text{ \AA}$

 $d(\text{O}-\text{O}) < 2.5 \text{ \AA}$

 $d(\text{O}-\text{O}) < 2.6 \text{ \AA}$

 $d(\text{O}-\text{O}) < 2.64 \text{ \AA}$


A new electrocatalyst prepared for this study, $\text{Na}_{0.67}\text{CoO}_2$, consists of two-dimensional CoO layers separated by Na layers (not shown). The Co ions (blue spheres) have four different positions (Co1-Co4), and the distorted Co-O octahedra have varying oxygen-oxygen (O-O) separations (thick red lines connecting red spheres). All of the O-O bonds are shorter than 2.64 \AA (the length of the corresponding bonds in a comparable material), and the shortest bonds are less than 2.40 \AA . It turns out that O-O separation has a strong effect on the oxygen evolution reaction (OER) in this material.

Enhancing the oxygen evolution reaction

The oxygen evolution reaction (OER) is the electrochemical mechanism at the heart of many processes relevant to energy storage and conversion, including the splitting of water to generate hydrogen fuel and the operation of proposed long-range batteries for electric vehicles. Because the OER rate is a limiting factor in such processes, highly active OER electrocatalysts with long-term stability are being sought to increase reaction rates, reduce energy losses, and improve cycling stability. Catalysts incorporating rare and expensive materials such as iridium and ruthenium exhibit good performance, but an easily prepared, efficient, and durable OER catalyst based on earth-abundant elements is still needed for large-scale applications.

Key insight: shorter O-O bonds

In an earlier study, a group led by John Goodenough (2019 Nobel laureate in chemistry) measured the OER activities of two compounds with similar structures: CaCoO_3 and SrCoO_3 . They found that the CaCoO_3 exhibited higher OER activity, which they attributed to its shorter oxygen-oxygen (O-O) bonds. Inspired by this, members of the Goodenough group have now analyzed a metallic layered oxide, $\text{Na}_{0.67}\text{CoO}_2$, which has an even more compact structure than CaCoO_3 .

X-ray diffraction (XRD) experiments performed at the Advanced Photon Source (APS) confirmed that the shortest O-O separation in $\text{Na}_{0.67}\text{CoO}_2$ is 2.30 \AA , compared to 2.64 \AA for CaCoO_3 . The researchers then compared the OER performance of $\text{Na}_{0.67}\text{CoO}_2$ with IrO_2 , Co_3O_4 , and $\text{Co}(\text{OH})_2$. They found

Scientific Achievement

With key data from the Advanced Light Source (ALS), researchers explained how a new, low-cost electrocatalyst enables an important oxygen reaction to proceed at an ultrafast rate.

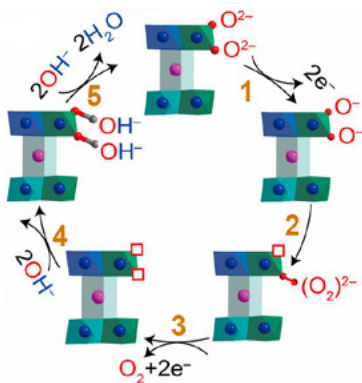
Significance and Impact

The work provides rational guidance for the development of better electrocatalysts for applications such as hydrogen-fuel production and long-range batteries for electric vehicles.

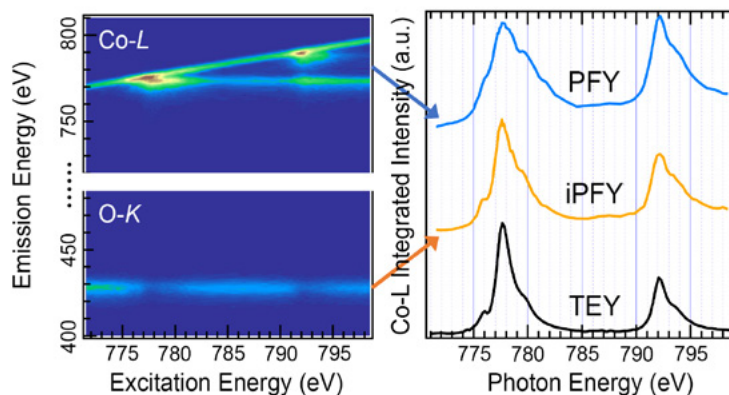
that $\text{Na}_{0.67}\text{CoO}_2$ exhibited the highest current density, the lowest overpotential (a measure of thermodynamic energy loss), and the most favorable Tafel slope (sensitivity of the electric current to applied potential). The $\text{Na}_{0.67}\text{CoO}_2$ also showed excellent stability under typical operating conditions.

A probe of valence and spin

To better understand how O-O bond lengths affect the OER, the researchers probed the Co valence and spin states using soft x-ray absorption spectroscopy (XAS) and mapping of resonant inelastic x-ray scattering (mRIXS) at ALS Beamline 8.0.1. With spectra extracted from the mRIXS data in various ways, both the chemical and spin states of the Co , in the bulk and on the surface, were derived and quantitatively analyzed. Thus, the mean



A new OER pathway on $\text{Na}_{0.67}\text{CoO}_2$ begins with interactions between neighboring oxygen ions in CoO_2 layers (steps 1-2 above). When the O-O bond length is small, this mechanism outpaces the conventional OER pathway.



Left: mRIXS data collected with incident x-rays scanning through the Co L-edge. Right: Spectra extracted from the mRIXS data in various ways; these were used to derive and quantitatively analyze both the chemical and spin states of the Co. PFY = partial fluorescence yield; iPFY = inverted PFY; TEY = total electron yield.

valence state of the Co was found to be 3.3+, and the ratio of the of the L_3 and L_2 edges revealed that the Co electron configuration was in a low-spin state, which is consistent with a more compact structure and intrinsically beneficial to OER stability.

Competing reaction rates

Based on the insights revealed by this new data, the researchers proposed an alternative OER mechanism to explain the ultrafast performance of $\text{Na}_{0.67}\text{CoO}_2$. Whereas conventional OER is initiated by interactions between surface anions and OH^- from the electrolyte solution, the new pathway starts with interactions between oxygen ions in neighboring CoO_2 layers. The reaction rate of this alternate pathway increases steeply as the O-O separation decreases, quickly outpacing the conventional route when O-O bonds are short. In total, the results demonstrate an invaluable array of tools and techniques that will greatly enhance future efforts to rationally design low-cost alternatives to precious-metal OER electrocatalysts.

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