Lattice oxygen coupling during water oxidation on an oxide electrocatalyst probed by X-ray and neutron techniques

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Understanding the mechanistic pathways of water oxidation, also referred to as the oxygen evolution reaction (OER), is essential to guide catalyst design and to advance sustainable energy technologies, as the inherently sluggish kinetics of the OER remain a fundamental bottleneck. In this work, we study the OER mechanism on a $Bi_{0.2}Sr_{0.8}CoO_{3-\delta}$ perovskite catalyst, which exhibits an exceptionally high OER activity. Through *operando* electrochemical mass spectrometry using an ^{18}O-isotope labeled catalyst, we observed that OER proceeds via the coupling of oxygen sites within the oxide lattice, marking the first direct experimental observation of such OER mechanism in a metal oxide catalyst. Further, a *quasi in situ* study of oxygen intercalation into the perovskite lattice, using a series of $Bi_{0.2}Sr_{0.8}CoO_{3-\delta}$ materials with a systematically controlled oxygen content, enabled us to track the structure of putative oxygen evolution reaction intermediates confined within the bulk oxide. By combining insights from Co K-edge and Bi L_3-edge X-ray absorption spectroscopy (XAS), O K-edge resonant inelastic X-ray scattering (RIXS), X-ray photoelectron spectroscopy (XPS), X-ray and neutron powder diffraction, and density functional theory (DFT) calculations, we observed that increasing oxygen content in $Bi_{0.2}Sr_{0.8}CoO_{3-\delta}$ leads to a concurrent reduction of cobalt sites and oxidation of lattice oxygen, ultimately resulting in the formation of O–O moieties within the catalyst lattice, which represent the key intermediate of the intramolecular oxygen coupling pathway of the OER. Our findings [1] redefine the mechanistic framework traditionally applied to oxide electrocatalysts by identifying the redox activity of lattice oxygen as a central design parameter. These results open new avenues for tuning catalytic activity beyond the conventionally utilized descriptors.

[1] D. A. Kuznetsov, *et al. ChemRxiv* (2026). DOI:10.26434/chemrxiv.15000244/v1.