

Unraveling the Geometrical Site Confinement in Iron-Doped Electrocatalysts Toward Water Oxidation

The use of X-rays is conducive to understand the surface mechanism operating in various applications and to deduce the pertinent systems.

The role of binary-metal ions in electrocatalysts has aroused considerable attention but remains under protracted debate. The existence of these controversies indicates that the behaviors of these metal ions in the electrolyte are poorly elaborated, especially for the orbital interaction between the metal ions (*i.e.* active sites) and the adsorbates during the catalytic reaction. From the viewpoint of the geometrical site in the lattice and the structural conversion, it is highly desirable to recognise how the material engineering and manipulation dominate the catalytic activities and structural stabilities. Toward this end, it is paramount to develop a technique *in situ* that allows one to identify the roles of these electrocatalysts under realistic conditions.

Hao Ming Chen (National Taiwan University) and his co-workers recently developed Fe-doped cobalt oxides as an efficient electrocatalyst for the oxygen-evolution reaction (OER).¹ Dynamic structural conversion is clearly evident from X-ray absorption spectra (XAS) recorded *in situ* at TLS 01C1 (Fig. 1(a) and 1(b)). The ratio of the coordination numbers of octahedral and tetrahedral sites gradually increases in the region of oxidation and subsequently decreases during the reduction, which indicates that the structural conversion is a dynamic equilibrium rather than an irreversible process. The authors clarified the distinctive geometric sites in spinel; Fe occupies the octahedral sites ($\text{Fe}^{3+}_{(\text{Oh})}$) and Co is confined to the tetrahedral site ($\text{Co}^{2+}_{(\text{Td})}$), resulting in a strikingly great activity. A further enrichment of Fe ions would occupy the tetrahedral sites to decrease the amount of $\text{Co}^{2+}_{(\text{Td})}$ and to deteriorate the OER activity. $\text{Fe}^{3+}_{(\text{Oh})}$ ions are hence proposed mainly to confine cobalt ions to the tetrahedral site so as to restrain the multipath transfer of cobalt ions during the dynamic structural transformation between spinel and oxyhydroxide, continuously activating the catalytic behavior of $\text{Co}^{2+}_{(\text{Td})}$ ions (Fig. 1(c)).

Chen's group also developed Fe-doped spinel (Co-Dom spinel and Fe-Dom spinel, named after the specific metal-oxide-dominated frames).² Recording $K_{\beta 1,3}$ high-energy-resolution fluorescence-detected X-ray absorption spectra (HERFD-XAS) *operando* with a small incident angle at NSRRC beamline SP12U1 of SPring-8, these authors observed oxygen directly interacting with 3d orbitals of Co ions rather than those of Fe ions. They concluded that the Co-Dom spinel evidently affected the oxidized behavior or coordinating environment of cobalt ions, which benefits the catalytic OER (Fig. 2(a) and 2(b)). Most importantly, the result indicates that the presence of Fe ions near the Co ions can significantly stabilize the Co ions with higher oxidation states, which might facilitate the formation of intermediates and further refer to an efficient path of OER. The results of HERFD *operando*, as shown in Fig. 2(c)–2(f), reveal a significant in-

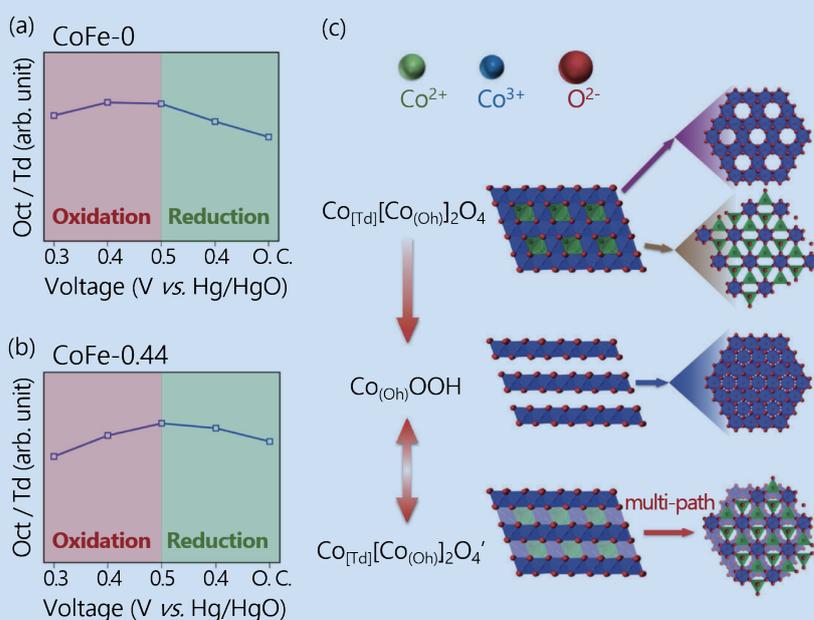


Fig. 1: Ratio of coordination numbers of octahedral and tetrahedral sites, extracted from XAS *in situ* for (a) CoFe-0 and (b) CoFe-0.44. The catalyst underwent oxidation and then reduction during the measurement *in situ*. O. C. means open circuit state. (c) Schematic representation of the multipath during a phase conversion in cobalt oxides. [Reproduced from Ref. 1]

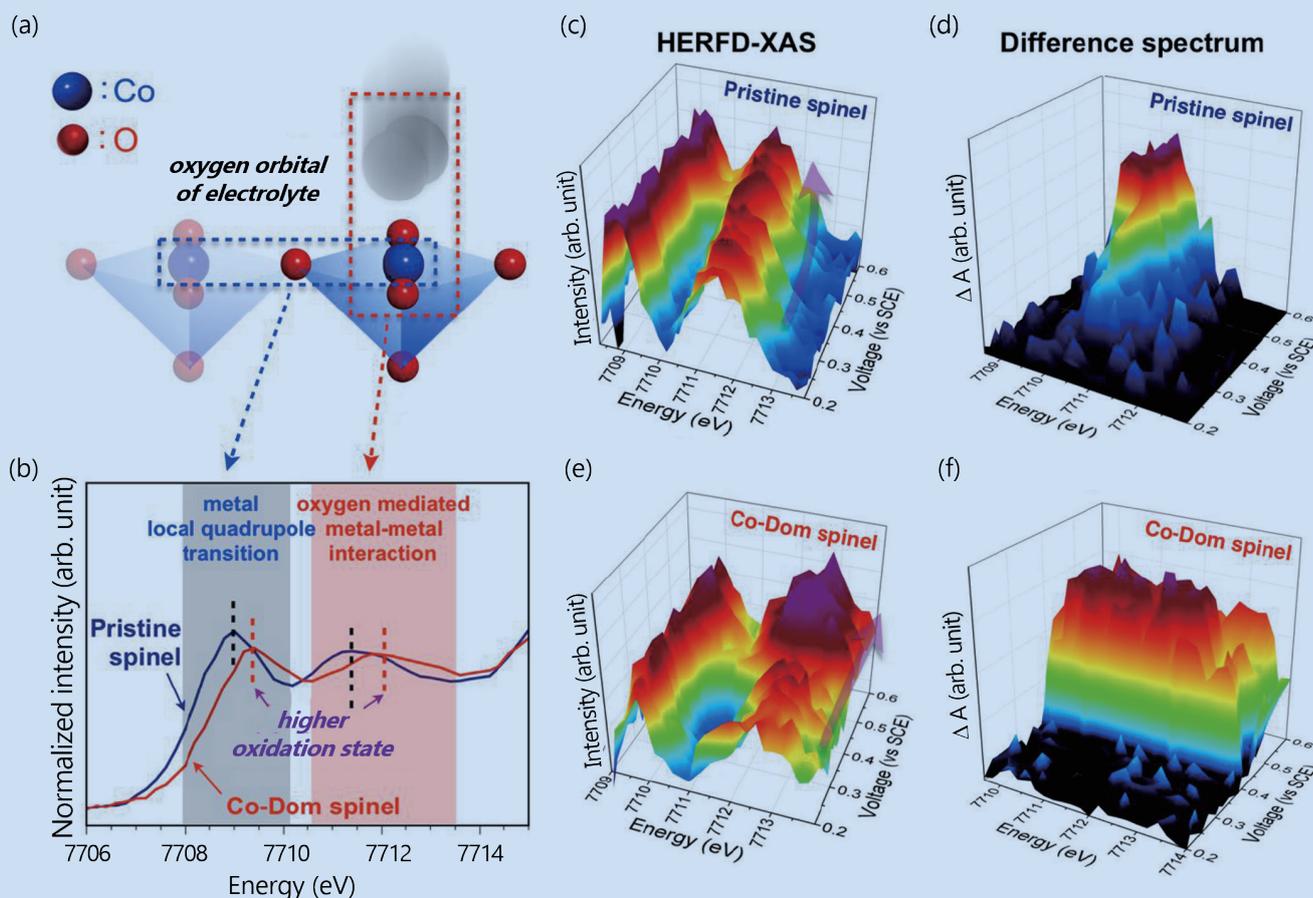


Fig. 2: (a) Schematic illustration of the interaction of a cobalt 3d-orbital of a catalytic surface with an oxygen 2p-orbital of the electrolyte. (b) High-energy-resolution fluorescence-detection X-ray absorption spectra of the Co K-edge for pristine spinel and Co-Dom spinel. HERFD-XAS *operando* and difference spectra of the Co K-edge for (c)–(d) pristine spinel and (e)–(f) Co-Dom spinel. [Reproduced from Ref. 2]

teraction between the electrolyte and Co ions during the catalysis. The authors observed also a different behavior with regard to the chemical state of the Co ion, thereby leading to a distinct path or intermediated state in OER. The Co-Dom spinel exhibited a substantially intense maximum of the oxygen-mediated metal-metal interaction with increasing applied voltage (*i.e.*, during OER), and verified a stronger orbital interaction between Co ions and O ions than in the pristine spinel. These results might be the key reason for the increased intrinsic catalytic activity of the Co-Dom spinel.

In summary, an introduction of iron into cobalt oxides and spinel systems has served a crucial function to enhance significantly the catalytic activity toward the oxygen evolution reaction. X-ray spectra, including conventional XAS and HERFD-XAS, were recorded *in situ* to unveil the catalytic nature of the complicated catalysts. In particular, the HERFD-XAS approach *operando* corresponding to the local orbital interaction at the reactant-catalyst interface can potentially offer

synergetic strategies toward recognising the chemical reactions or reaction paths in various fields. (Reported by Yan-Gu Lin)

This report features the work of Hao Ming Chen and his co-workers published in (1) Adv. Energy Mater. **8**, 1701686 (2018), and (2) *J. Am. Chem. Soc.* **140**, 17263 (2018).

TLS 01C1 SWLS – EXAFS

SP12U1 U32 – Inelastic X-ray Scattering

- XANES, EXAFS
- Materials Science, Chemistry, Condensed-matter Physics, Environmental and Earth Sciences

References

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