Identification of Stabilizing High-Valent Active Sites by Operando High-Energy Resolution Fluorescence-detected X-ray Absorption Spectroscopy for High Efficient Water Oxidation[1]

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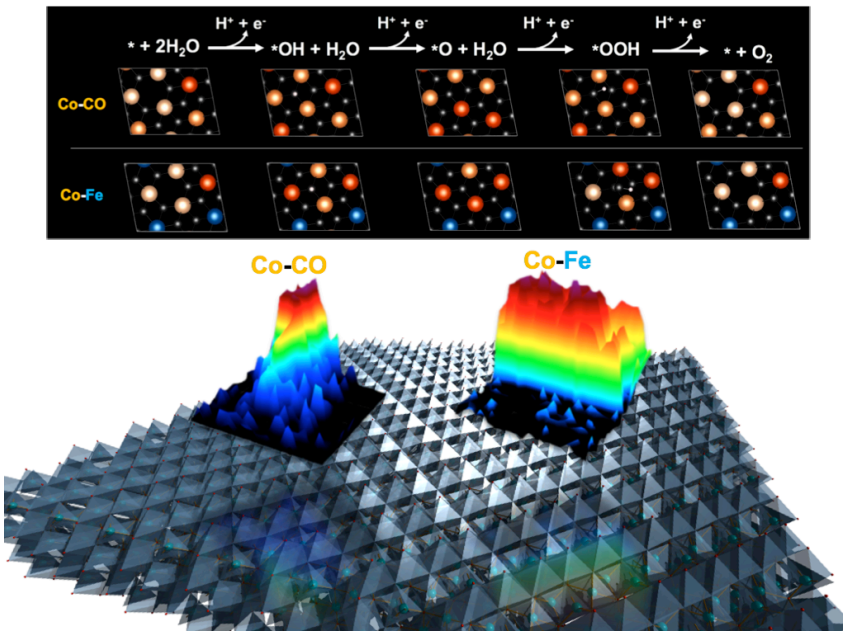
Abstract

Composite electrocatalysts have exhibited high activities toward water electrolysis,[2] but the catalytically active sites really in charge of the reaction are still debatable while the conventional in situ X-ray spectroscopies are not capable of conclusively identifying the interaction of these materials with the electrolyte because of the complexity of catalysis. In this work, by utilization of operando $K_{\beta 1,3}$ high-energy resolution fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS) with a small incident angle, the operando quadrupole transition obviously showed that oxygen directly interacted with 3d orbitals of Co ions rather than that of Fe ions. Most importantly, Fe ions can promote the stabilization of the Co ions under a higher valent state during water oxidation, which may lead to a stable intermediate of reactant and its superior intrinsic activity. Accompanied by the first-principle calculations, the intermediates between 3d orbitals for surface Co ions and O 2p orbitals for the attaching hydroxide ions were ascribed to this orbital hybridization. Because of the unvaried structural features in conventional in situ techniques, operando HERFD-XAS revealed the remarkable change of chemical status to correlate with the orbital interaction rather than with the structural variation. This operando HERFD-XAS approach corresponding to the local orbital interaction in reactant/catalyst interface can potentially offer synergetic strategies toward realizing the chemical reactions or reaction pathways in various fields.

Keywords – water oxidation catalyst, operando HERFD, in-situ XRD, in-situ XAS.

References

[1]Hung, S.-F.; Chan, Y.-T.; Chang, C.-C.; Tsai, M.-K.; Liao, Y.-F.; Hiraoka, N.; Hsu, C.-S.; Chen, H. M. Identification of Stabilizing High-valent Active Sites by *Operando* High-energy Resolution Fluorescence-detected X-ray Absorption Spectroscopy for High Efficient Water Oxidation. *J. Am. Chem. Soc.* **2018**, *140,* 17263-17270.
[2]Hung, S.-F.; Hsu, Y.-Y.; Chang, C.-J.; Hsu, C.-S.; Suen, N.-T.; Chan, T.-S.; Chen, H. M. Unraveling Geometrical Site Confinement in Iron-Doped Electrocataltsts toward Oxygen Evolution Reaction. *Adv. Energy Mater*. **2018**, *8*, 1701686.



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