

PTB7 crystallization and multi-length-scale PC₇₁BM dispersion for the appropriate aggregation and networks. The subsequent dipping treatment with SH-na further modified the active layer morphology for a surface more enriched in PC₇₁BM and better PC₇₁BM networks in the bulk film, hence resulting in an improved device performance. (Reported by Yan-Gu Lin)

This report features the work of Show-An Chen and his co-workers published in Adv. Funct. Mater. 26, 3094 (2016).

TLS 23A1 IASW – Small/Wide Angle X-ray Scattering

- SAXS, WAXS
- Soft Matter, Protein Crystallography, Materials Science, Atomic and Molecular Science

| Reference |

1. H. J. Jhuo, S. H. Liao, Y. L. Li, P. N. Yeh, S. A. Chen, W. R. Wu, C. J. Su, J. J. Lee, N. L. Yamada, and U. S. Jeng, *Adv. Funct. Mater.* **26**, 3094 (2016).

Peering Deep inside an Electrocatalyst

The distinct kinetics and electrochemical reactivities of Co²⁺_{Td} and Co³⁺_{Oh} toward OER in spinel Co₃O₄ were identified with a combination of operando X-ray absorption spectra and electrochemical impedance spectral techniques.

The electrolysis of water provides a promising way to supply and to store clean and sustainable energy; two half reactions are hydrogen evolution (HER) and oxygen evolution (OER). Among these two reactions, water oxidation is the rate-determining step because of a thermodynamically uphill reaction that involves a species Co³⁺_{Oh} stepwise four-electron transfer, which typically requires a large overpotential to drive the reaction. To develop efficient OER electrocatalysts becomes extremely important. Spinel cobalt oxide (Co₃O₄) is an earth-abundant and efficient OER catalyst with competitive activity that has been extensively studied to replace noble-metal-based catalysts. Its catalytic activity has been discovered to depend sensitively on the exposed crystal facets, which might influence the adsorption or desorption of reactants or products. Basically, spinel Co₃O₄ comprises geometric cobalt ions of two types with distinct oxidation states: one Co²⁺ ion in a tetrahedral site and two Co³⁺ ions in an octahedral site, denoted Co²⁺_{Td} and Co³⁺_{Oh}, respectively. The populations of Co²⁺_{Td} and Co³⁺_{Oh} on varied exposed facets of Co₃O₄ nanostructures have been demonstrated to be the key to influence the catalytic performance. Previous authors have proposed that the electrochemical OER performance of spinel Co₃O₄ is dependent on also the site geometry, in which Co³⁺_{Oh} of greater oxidation number should dominate the water oxidation, whereas Co²⁺_{Td} is inactive, but the chemical environment of Co₃O₄ is contributed by both Co²⁺_{Td} and Co³⁺_{Oh} species; more importantly, such an environment is dynamically variable during electrocatalysis with an applied bias. Without conclusive

evidence, the OER active sites in Co₃O₄ remain elusive.

In this work¹, to differentiate the catalytic active sites for water oxidation in spinel Co₃O₄, catalytically inactive Zn²⁺ and Al³⁺ with electronic configuration *d*⁰ replaced Co²⁺ and Co³⁺ in their corresponding tetrahedral and octahedral sites, respectively. To disclose the real-time OER activities of substituted cobalt oxides, Hao Ming Chen (National Taiwan University), Bin Liu (Nanyang Technological University) and Ting-Shan Chan (NSRRC) cooperatively measured operando X-ray absorption spectra at **TLS 01C1** and operando electrochemical impedance spectra.

Extended X-ray absorption fine structure (EXAFS) was recorded to probe the variation of the chemical environment on the catalyst during OER using a home-made cell in operando. **Figures 1(a)-1(c)** display Co K-edge spectra, which show that the corresponding interatomic distances of Co³⁺_{Oh} and Co²⁺_{Td} to their neighboring atoms in all catalysts remain nearly constant in a voltage range between 1.2 and 1.8 V vs. RHE, indicating a highly stable bulk structure of this spinel, but a slightly compressed Co-O bond was still observed in Co₃O₄ during OER (**Fig. 1(d)**), indicating a partial oxidation of the catalytic surface. Notably, the shrinking of the Co-O bond with an applied bias was observed for only Co²⁺_{Td}-predominated CoAl₂O₄, not ZnCo₂O₄ (**Fig. 1(d)**). The corresponding *k*³-weighted *k*-space spectra also reveal a variation between 1.0 and 1.8 V vs. RHE in Co₃O₄ and CoAl₂O₄. The Co K-edge EXAFS spectra (**Fig. 1(e)**) show that the inten-

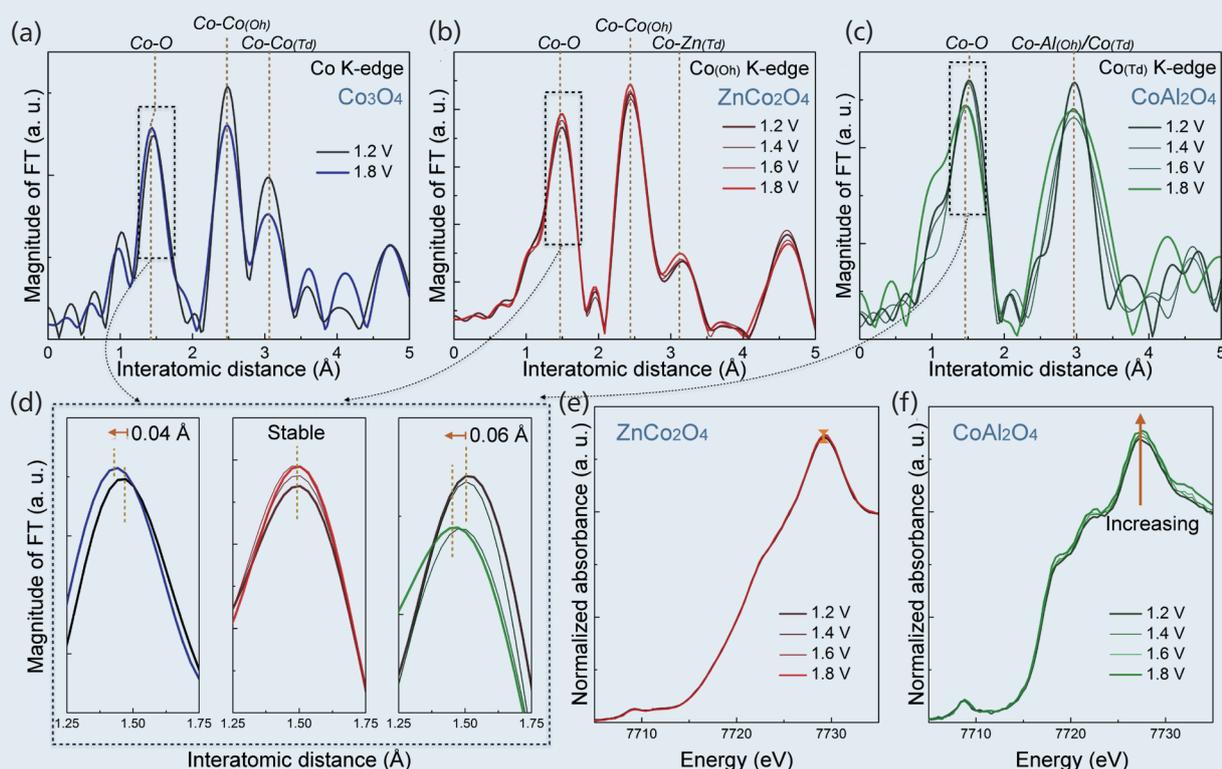


Fig. 1: In operando X-ray absorption spectra. (a)–(c) Co K-edge EXAFS spectra for Co_3O_4 , ZnCo_2O_4 , and CoAl_2O_4 , in which the applied voltage is referred to RHE. (d) Enlarged Co K-edge EXAFS spectra on the Co–O interatomic distance for Co_3O_4 (blue), ZnCo_2O_4 (red), and CoAl_2O_4 (green). (e)–(f) Normalized in operando Co K-edge XANES spectra for ZnCo_2O_4 and CoAl_2O_4 . [Reproduced from Ref. 1]

sity of the white line remains constant for ZnCo_2O_4 , but increases for CoAl_2O_4 with increasing applied positive bias (**Fig. 1(f)**), indicating an accumulation of positive charge on cobalt ions of CoAl_2O_4 ; *i.e.*, $\text{Co}^{2+\text{Td}}$ with an initially small oxidation state can release electrons under an applied bias, which can facilitate interaction with oxygen intermediates on the catalyst surface. This electron-releasing and oxygen-adopting process indicates the formation of CoOOH , which acts as the main active sites in the turnover-limiting path for water oxidation on Co_3O_4 . As compared with reported phosphate-containing cobalt oxide (or Co–Pi), in which the octahedral Co center in a cubane structure can be oxidized to Co(IV) in the OER cycle involving a chemical turnover-limiting process of CoOOH formation, this work reveals that species $\text{Co}^{3+\text{oh}}$ is inactive relative to $\text{Co}^{2+\text{Td}}$ in Co_3O_4 spinel. Based on the facts of the present results, it is concluded that, to form the CoOOH intermediate species, the oxidation of an active Co ion is the critical process; $\text{Co}^{2+\text{Td}}$ is disclosed to be the active species in Co_3O_4 , which can be oxidized under an applied anodic bias. The positive charge accumulated within the catalyst can thus greatly assist the formation of CoOOH on the Co_3O_4 surface.

In summary, the distinct kinetics and electrochemical reactivities of $\text{Co}^{2+\text{Td}}$ and $\text{Co}^{3+\text{oh}}$ toward OER in spinel

Co_3O_4 were identified. $\text{Co}^{2+\text{Td}}$ in Co_3O_4 is capable of releasing electrons under an applied bias, promoting the affinity for oxygen ions on the catalytic surface to form CoOOH , which acts as the main active site for OER. $\text{Co}^{3+\text{oh}}$ -predominant catalyst ZnCo_2O_4 , tends to bond stably with $-\text{OH}$ groups, thus limiting its catalytic activity. The importance of in operando investigations on electrocatalysis for instantaneous probing of the real-time electrochemical kinetics and surface reactions is particularly emphasized. (Reported by Yan-Gu Lin)

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TLS 01C1 SWLS – EXAFS

- XAS
- Materials Science, Chemistry, Environmental and Earth Science, Surface, Interface and Thin Films, Chemical Engineering

| Reference |

1. H. Y. Wang, S. F. Hung, H. Y. Chen, T. S. Chan, H. M. Chen, and B. Liu, *J. Am. Chem. Soc.* **138**, 36 (2016).