

Operando-captured O-529 eV signal: an indicator of active phase formation below OER potential

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Unbearable to the high catalytic potentials, most materials undergo either reversible or irreversible structural reconstruction during oxygen evolution reaction (OER) electrocatalysis, involving valence changes as well as coordination alternation of both metal and oxygen active sites^[1]. Such potential-dependent evolution happening on the local surface brings about certain challenges but also necessity to explore in-situ structure-performance relations^[2]. However, corresponding researches prove intractable to reach a consensus due to universally undeveloped operando characterization techniques^[3-4].

Among all kinds of non-noble metal alkaline OER catalysts, NiM (M = Fe, Mn, Co)-based layered double hydroxides (LDH) enjoying highly controllable structure, intensive host-guest interactions and well-dispersed single-atomic sites, have long served as prevalent alternatives with economic advantages over noble metal-based ones^[5]. Considering the widely-accepted reversible phase transformation process that usually takes place in NiM LDH systems, elucidating the dynamic evolution of both geometric and electronic structures of the active metal centers, nickel (Ni), as well as the ligands (namely O species here) along OER reaction coordinate, is pivotal for gaining a deep understanding of catalytic mechanism^[6]. Nonetheless, exclusive application of non-operando (including ex-situ) methods fail to capturing such transient signals, resulting in ambiguous or even incorrect interpretations to the structural conversion, thereby to some extent impeding the rational design of high-efficiency OER catalysts.

Recently, Prof. Peter Strasser and co-workers employing operando X-ray adsorption spectroscopy (XAS) combined with computational methods, commendably solved this puzzle. By fully deciphering the structural evolution of NiM LDH below and above OER redox potentials, they shed light on the relationship between the structural transition to active γ -phase and authentic OER performance. Specifically, they captured operando XAS spectra pertaining to O K-edge, discovering that upon the transformation of NiM LDH from a non-conductive α -phase under a non-catalytic potential (+1.15 V vs. RHE) to a conductive γ -phase under a catalytic

condition (+1.45 V vs. RHE), an extra peak emerges at 528.7 eV, a signal that can be referred as O-529 eV^[7]. The total fluorescence yield (TFY) of this signal was then tracked along with cyclic voltammetric sweeping (Figure 1a). As shown in Figure 1a, the extremum of the TFY derivative curves of anodic and cathodic scans show up at ~ 1.42 V and ~ 1.31 V (vs. RHE), respectively, well according with the ascension and descension of the current signal. Such good coincidence can also be conceived with the appearance of another peak situated at 856.2 eV referring to the formation of Ni⁴⁺ species (Figure 1b). Subsequently, the particular O-529 eV signal was investigated through DFT-guided XAS simulation, and was proved to exclusively indicate the formation of active γ -phase (Figure 1c), which mainly stems from the three-coordinated terrace O sites (μ_3 -O) within the γ -NiM LDH bulk, rather than any kinds of oxygenated intermediates adsorbed on the surface that have long been reckoned in this area.

As such, a dovetailing relation was established that the redox transition of Ni²⁺/Ni⁴⁺ actually happens simultaneously with the presence/absence of O-529 eV species and the upward/downward fluctuation of OER current, implying the completed formation of γ -phase below OER potential. Despite of the crucial role of O-529 eV signal as an important indicator to declare the phase conversion, the team clarified that the inclination of forming γ -phase shows limited relations to the OER intrinsic activity, suggesting that γ -phase with Ni⁴⁺ and O-529 eV species serves only as a necessary but not a sufficient prerequisite for NiM LDH to catalyze OER.

Based on the as-studied NiM LDH anodes, the authors further reported the preparation of directly catalyst-coated membrane (CCM) using wet-film bar-coating technique. They used an adhesive foil to minimize membrane swelling during the coating of the second catalyst layer, and thereby achieved an impressive anion-exchange membrane water electrolyzer (AEMWE) performance to deliver >5 A cm⁻² at <2.2 V. Notably, this AEMWE with ohmic drop correction trails Ir-based proton-exchange membrane water electrolyzer (PEMWE) by just 150 mV at 4 A cm⁻² (Figure 1d), showcasing promising practical potentials with substantial cost benefit analysis (CBA) benefits^[8].

In summary, this study employed a combination of operando X-ray absorption spectroscopy and theoretical calculations to precisely elucidate the evolution of central metal atoms and O ligands of NiM-LDH materials under OER poten-

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Received 12 December 2024; Accepted 17 December 2024; Published online

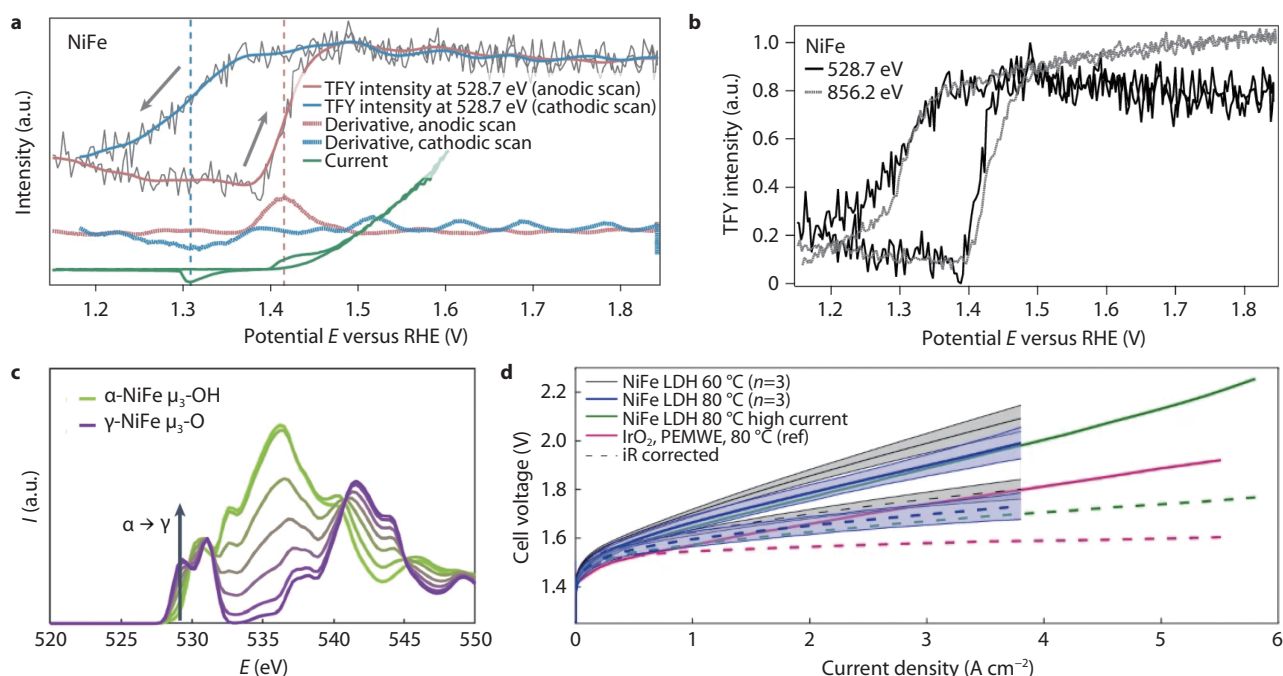


Fig. 1 **a** Comparison of the TFY intensity at the maximum of the pre-edge feature (528.7 eV) as a function of the applied potential during CV, with its first derivative and the corresponding CV for NiFe LDH. **b** Comparison of the TFY signal at 528.7 eV and at 856.2 eV for NiFe LDH. The measurements were conducted in 0.1 M KOH at room temperature. **c** Average O K-edge (normalized) of all oxygen atoms at the hollow sites of α - and γ -phases, with the combination of various $\alpha/(\alpha+\gamma)$ ratios of 0.1, 0.3, 0.5, 0.7 and 0.9. **d** Polarization curves of CCM-based AEMWE single cells with 1.0 ± 0.2 mg_{NiFe-LDH} cm⁻² and 0.5 ± 0.1 mg_{Pt} cm⁻² in 1 M KOH. The magenta line represents the state-of-art PEMWE polarization [8]. Shaded areas show 95% confidence intervals ($n=3$; individual cells). Dashed lines denote high frequency resistance (HFR)-corrected curves.

tial. An O-529 eV XAS signal was pointed out as an indicator of the formation of active γ -phase, and was proved paralleling well with the Ni²⁺/Ni⁴⁺ transition as well as the OER current response. This discovery shakes the cobwebs off the ambiguous interpretations about the operando O signals of NiFe-based LDH materials, offers fresh perspectives on unraveling the structure-activity relationships, and provides meaningful guidance for the development of non-noble metal OER catalysts. On the other hand, the authors introduced an innovative CCM preparation method, advocated a large-scale production of Ir-free AEMWE cells, and whereby highlighted the potential of NiFe-based LDH materials as low-cost and effective anodes toward AEMWE technology.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

1. S. Chen, S. Zhang, L. Guo, L. Pan, C. Shi, X. Zhang, Z. -F. Huang, G. Yang, J. -J. Zou, *Nat. Commun.*, 2023, 14, 4127
2. T. Li, O. Kasian, S. Cherevko, S. Zhang, S. Geiger, C. Scheu, P. Felfer, D. Raabe, B. Gault, K. J. J. Mayrhofer, *Nat. Catal.*, 2018, 1, 300
3. Z. Chen, Q. Fan, J. Zhou, X. Wang, M. Huang, H. Jiang, H. Cölfen, *Angew. Chem. Int. Ed.*, 2023, 62, e202309293
4. S. Zuo, Z.-P. Wu, H. Zhang, X. W. Lou, *Adv. Energy Mater.*, 2022, 12, 2103383
5. D. Zhou, P. Li, X. Lin, A. McKinley, Y. Kuang, W. Liu, W.-F. Lin, X. Sun, X. Duan, *Chem. Soc. Rev.*, 2021, 50, 8790
6. Z. Wang, W. A. Goddard, H. Xiao, *Nat. Commun.*, 2023, 14, 4228
7. M. Klingenhof, H. Trzesniowski, S. Koch, J. Zhu, Z. Zeng, L. Metzler, A. Klinger, M. Elshamy, F. Lehmann, P. W. Buchheister, A. Weisser, G. Schmid, S. Vierrath, F. Dionigi, P. Strasser, *Nat. Catal.*, 2024, 7, 1213
8. M. Bernt, A. Siebel, H. A. Gasteiger, *J. Electrochem. Soc.*, 2018, 165, F305