Review Article

Enlightening the journey of metal-organic framework (derived) catalysts during the oxygen evolution reaction in alkaline media via operando X-ray absorption spectroscopy

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Abstract
The development of catalysts with enhanced activity for the oxygen evolution reaction (OER) compared to the traditionally used metal oxide catalysts is crucial for further commercialization of electrolyzers. Because of their high surface area and adjustable pore structure, metal-organic framework (MOF)-based catalysts represent a promising alternative. During the OER in alkaline media, the initial MOF structure is susceptible to transformations including the decomposition of the organic backbone and/or the formation of oxide, hydroxide and oxyhydroxide intermediates. Hence, operando characterizations of MOF catalysts during OER are essential to understand the material's progressive changes and extract the OER catalytic mechanism. This article discusses existing operando X-ray absorption spectroscopy studies of MOF(-derived) catalysts during OER and extracts important parameters for future research regarding operando X-ray absorption spectroscopy characterizations of MOFs during alkaline electrolysis.

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Keywords
Electrolysis, Water splitting, XAS, Operando.

Introduction
Because of the increased focus on renewable energy sources, often intermittent by nature, efficient energy conversion and storage systems become more important [1]. The excess energy conversion into hydrogen via water electrolysis is a promising technique, as hydrogen has a high combustion enthalpy without entailing carbon emission [2]. Focusing on further commercialization of electrolyzers, the oxygen evolution reaction (OER) is of special interest as it exhibits slow reaction kinetics and large overpotentials [3]. Hence, the development of highly OER active catalysts is crucial [4–6]. In that regard, metal-organic framework (MOF)-based catalysts are very promising because of their adjustable morphology and high surface area [7–12]. MOFs generally consist of metal atoms/clusters and organic ligands, which link the metal units to other metal centers forming a porous structure [13,14], where the active metal sites are homogeneously dispersed [9]. MOFs containing Ni, Co, and Fe exhibit impressive OER activities and performance stabilities [15–17]. Besides pristine MOFs, often MOF-derived catalysts synthesized by modification of pristine MOFs, are investigated [18,19]. Via pyrolysis in an inert atmosphere, the organic ligands are converted into porous carbons, whereby the porous structure of the pristine MOF is mostly maintained, and the metal ions are transformed into metal or metal oxide nanoparticles embedded into the carbon matrix. These MOF-derived catalysts exhibit improved electroconductivity while maintaining the favorable pristine MOF morphology or even advanced morphologies as, for example, nanosheets [11].

However, there are also challenges when applying MOF catalysts in OER. The two main issues are the inferior stability of several MOF structures in polar solvents and the poor electrical conductivity [10,11]. The electrical conductivity can be enhanced, (i) as described previously, by MOF pyrolysis and transformation into nanosheets or (ii) by the introduction of a secondary metal to tune the electronic structure [20,21]. Another approach is growing MOFs directly on conductive substrates to achieve binder-free catalysts with enhanced conductivity and activity [20,22,23]. Many recent reviews focus on the comparison of different MOF(-derived) structures and their OER performance [10,11,21,24–27]. It is emphasized that MOFs undergo transformations in the
conditioning phase and during OER, whereby the porous structure collapses and/or the metal clusters evolve into metal oxides, hydroxides, and oxyhydroxides [10,11,24,25]. As \textit{ex situ} characterizations cannot detect the actual physicochemical properties of the catalyst materials under operation, \textit{in situ} and especially operando characterization methods are needed to analyze the structural and electronic transformations of MOF(-derived) catalysts during OER. Those characterizations enable a deeper understanding of the OER catalytic mechanism of MOFs and, hence, reveal further research perspectives for MOF catalyst development for OER.

An extensive overview of different operando characterization methods for MOF catalysts is published by Kornienko [28]. Operando characterizations during OER in alkaline media mainly include operando Raman, Fourier-transformed infrared and X-ray absorption spectroscopy (XAS), respectively [29–31]. XAS is especially powerful, as it enables the study of both the electronic structure and the chemical environment of a specific element [32–34]. Thus, this perspective focuses on recent operando XAS characterizations of MOF(-derived) electrocatalysts during OER in alkaline media.

**Analysis of recent operando XAS studies of MOFs in OER**

In 2016, Zhao et al. [31] provided the first detailed discussion regarding operando XAS measurements of MOF catalysts during OER in an alkaline electrolyte. They analyzed ultrathin NiCo-MOF nanosheets (NiCo-UMOFNs) based on ligands synthesized from benzene-dicarboxylic acid (BDC), which exhibited a lower overpotential and improved performance stability than a commercial RuO$_2$ catalyst studied under the same conditions. The catalyst stability under X-ray irradiation was investigated by collecting XAS spectra at Ni and Co K-edge (in air and in 1 M KOH) after 15, 30 and 45 min, without applied potential and no significant changes were detected. At applied potentials of 1.43 V$_{\text{RHE}}$, 1.48 V$_{\text{RHE}}$ and 1.53 V$_{\text{RHE}}$, the NiCo-UMOFNs exhibited a larger ratio of oxidized Ni atoms and more coordinatively unsaturated Co sites than pristine NiCo-MOFs. According to their calculations, the improved OER performance of NiCo-UMOFNs resulted from better adsorption of OER intermediates at the coordinatively unsaturated metal sites. Moreover, the catalytic activity of the NiCo-UMOFNs was compared with a simple blend of Ni- and Co-MOF nanosheets. Coupling density functional theory (DFT) calculations and X-ray photoelectron spectroscopy (XPS) measurements, it was concluded that partial electron transfer from Ni$^{2+}$ to Co$^{2+}$ led to the improved OER performance of the NiCo-UMOFNs. This study focused on the comparison of the developed MOF nanosheet catalyst with pristine MOFs and single-metal MOF nanosheets. In contrast, the Ni oxidation and structural transformation under operative conditions for NiCo-MOF-74 and NiFe-MOF-74, both with varying metal ratios, were analyzed in detail using operando XAS by Zhao et al. in 2020 [35]. Among the studied MOF catalysts, Ni$_{0.9}$Fe$_{0.1}$-MOF-74 and Ni$_{0.5}$Co$_{0.5}$-MOF-74 were most active toward OER, both surpassing the OER performance of a commercial

![Figure 1](https://example.com/figure1.png)

**Figure 1**

Ni K-edge extended X-ray absorption fine structure (EXAFS) data of the two reference materials (β-Ni(OH)$_2$ and γ-NiOOH) and the analyzed Ni$_{0.5}$Co$_{0.5}$-MOF-74 in a pristine state at 1.1, 1.3 and 1.5 V$_{\text{RHE}}$. x represents the phase shift. A transfer from the initial state via a hydroxide state into an oxyhydroxide analog with increasing potential is presented. Reprinted by permission from Springer Nature: Springer Nature, Nature Energy, ‘Structural transformation of highly active metal–organic framework electrocatalysts during the oxygen evolution reaction’, Shenlong Zhao et al. Springer Nature License (2020) [35].
RuO2 catalyst at the same conditions. Before conducting XAS measurements of Ni0.5Co0.5-MOF-74, possible beam-induced damage was precluded by testing beam stability in the same manner as described previously, comparing the initial X-ray absorption near-edge spectroscopy spectra with those after 30 min and 60 min of X-ray irradiation. Then, operando XAS measurements were carried out in three different potential stages, the first stage at 1.1 V_RHE, the second state at 1.3 V_RHE as a transition stage and the catalytic stage at 1.5 V_RHE. As depicted in Figure 1, Zhao et al. [35] discovered two consecutive steps of dynamic structural transformation. First, the Ni clusters of Ni0.5Co0.5-MOF-74 changed into hydroxide analogs at 1.1 V_RHE, and second, oxyhydroxide analogs were formed in the catalytic state. Interestingly, the structural transformation was reported to be reversible and the pristine Ni0.5Co0.5-MOF-74 electronic and local structure was restored after 15 days of storage in air. Therefore, it was concluded that the structural transformation did not originate from MOF crystal structure decomposition. Moreover, the Ni–Co interaction was analyzed further by varying the Ni/Co ratio showing that this ratio influences the potential at which the phase transition takes place, whereby the introduction of Co enhanced the Ni oxyhydroxide formation. As the two-step structural reconstruction of the NiCo-MOF-74 is crucial for the OER mechanism, the Ni/Co ratio has been recognized as an important parameter influencing the catalytic activity of NiCo-MOF-74. A similar influence of the Ni/Fe ratio on the NiFe-MOF-74 OER activity and a similar two-stage transition under OER conditions, including the reversibility of the structural transformation, were observed [35]. This of special interest as it is in contrast to findings regarding the influence of Fe incorporation into Ni oxides, where Fe stabilized the Ni2+ state and hence, inhibited oxyhydroxide formation on Ni [36]. This contradiction underlines the importance of operando analysis of MOF-(derived) structures to study phase transformations during OER in order to extract important mechanisms determining their OER activity.

Ji et al. [37] studied NiFe-MOFs based on BDC and monocarboxylic acids, which were used as non-bridging ligands to produce a lattice-strained NiFe-MOF (LS-NiFe-MOF) with an altered electronic configuration. LS-NiFe-MOFs with 6% lattice expansion exhibited a stable current density for 5.5 h at 1.5 V_RHE and lower overpotentials than a commercial IrO2 catalyst under the same conditions. Operando XAS studies were conducted to analyze the change in the electronic structure of the LS-NiFe-MOFs and — in accordance with the findings of Zhao et al. [35] — the formation of an *OOH analog on the Ni3+/Ni4+ during OER was discussed, whereas Fe was determined to be OER inert. Combination of operando XAS and operando Fourier-transform infrared experiments with DFT calculations suggested that the lattice strain induced a decreased occupation of the Ni 3d eg orbitals because of a partial electron transfer from Ni to Fe. As this was calculated to result in improved adsorption of the second OH' for *OOH formation, the induced lattice strain led to an improved OER performance due to faster *OOH formation at the active Ni sites of the LS-NiFe-MOF catalyst. Another study analyzing the bimetallic interaction of Fe and Ni in a MOF-derived structure during OER was conducted by Zhao et al. in 2021 [38]. After pyrolysis of ZIF-67, a controlled 3D carbon network (C-MOF) was formed, and layered double hydroxide nanodots (LDH-NDs) were anchored to this network. The synthesis procedure is schematically depicted in Figure 2. The NiFe-catalyst exhibited a superior OER activity and performance stability compared to conventional (non-MOF-derived) LDH-nanosheets, the pure carbonized MOF and commercial RuO2 under the same conditions. Operando XAS measurements were performed at an open-circuit voltage and 1.45 V_RHE comparing the obtained LDH-NDs@C-MOF catalyst with LDH-nanosheets. Thereby, Zhao et al. [38] discovered oxidation of Ni2+ at 1.45 V_RHE in the MOF-derived catalyst, whereas LDH-nanosheets maintained the lower Ni oxidation state and exhibited lower OER activity. Further extended X-ray absorption fine structure (EXAFS)-FT study of the Ni and Fe K-edge revealed an increased structural distortion in the LDH-NDs@C-MOF. In combination with further XPS studies and DFT calculations, it was concluded that the favorable OER performance of the MOF-derived catalyst resulted from an optimized binding strength of the adsorbed intermediates because of a Fe–Ni coupling effect, where the charge transfer from Fe3+ to Ni2+ through an O bridge was revealed. Hence, the following effects were summarized as reasons for the enhanced OER performance: (1) increased number of catalytic sites (edge defects and vacancies) and high surface area at nanodots compared to nanosheets, (2) the porous carbon network enhanced electron transfer and diffusion of reactants and products, and (3) the Fe–Ni coupling effect affects the binding strength of adsorbed intermediates.

Another option to enhance the OER activity is using functional groups to alter the electronic configuration of the active metal sites of MOFs. This strategy was investigated by Cheng et al. [23] through the introduction of OER inert Au nanocrystals into a FeNiCo-MOF synthesized from BDC and directly grown on nickel plates. Au-decorated FeNiCo-MOFs exhibited an enhanced OER activity and stability compared to FeNiCo-MOF without Au decoration. The authors suggested that the high electronegativity of the Au nanocrystals led to more positively charged metal centers of the MOF as Au pulled electrons from these centers. Hence, less applied potential was needed to initiate the OER. Furthermore, the interaction between
the three different metals composing the MOF catalyst (Fe, Ni and Co) during the OER was analyzed using operando XAS. Comparing measurements at the opencircuit voltage and 1.73 \text{V}_{\text{RHE}} as presented in Figure 3, the increasing Co and especially Ni K-edge positions with increasing applied potential suggested that only Co and Ni were the OER active metal centers. As the edge position increase was reversible, it was concluded that Co\textsuperscript{3+}/Co\textsuperscript{4+} and Ni\textsuperscript{3+}/Ni\textsuperscript{4+} might only occur at high potentials, which lead to the transformation of a Ni hydroxyl analog into a Ni oxyhydroxide analog. Further analysis of mono- and bimetallic MOFs ensured that trimetallic FeNiCo-MOFs displayed superior OER performance, while Fe could enhance the catalytic OER activity of Ni more effectively than Co. This study shows how the operando methods can lead to an increased understanding of the electronic and local structural transformations in MOF materials, which appears to be crucial for high OER activity.

Discussion of recent studies and future perspective
The discussed studies provide several strategies to enhance the MOF OER activity, e.g. structural or electronic transformations of the MOF via production of nanosheets/nanodots or the introduction of lattice strain or metal doping. However, in all cases, operando XAS measurements suggest that the Ni oxidation into Ni oxyhydroxide species is the key parameter promoting the OER activity. Thereby, it is important to consider that before most of the discussed XAS measurements, the working electrode was electrochemically conditioned by cyclic voltammetry in the OER potential region \cite{23,31,35,37,38}, which might already have promoted the structural transformation of the Ni centers. This is important when analyzing the listed OER activities and correlating them with operando XAS findings because even though most studies claim the reversibility of the structural transformation of the Ni centers, for example, Zhao et al. \cite{35} state that this 'self-healing' takes 15 days in air.

Moreover, the OER activity comparison with commercial IrO\textsubscript{2} or RuO\textsubscript{2} catalysts should be studied critically, as most studies do not define the analyzed commercial catalysts in detail. For example, different surface areas, which have a significant impact on the measured OER activity, are not evaluated \cite{31,35,37,38}.

The stability of the catalysts under X-ray irradiation should always be studied before conducting operando XAS measurements or be analyzed by comparison of K-edge spectra before and after the experiments, as presented by Ji et al. \cite{37}. Unfortunately, some studies did not consider this important aspect \cite{23,38} and even more studies do not specify the duration of their operando XAS measurements to enable the reader to evaluate the relevance of the stability tests conducted.

Many MOFs are synthesized with ultrasonication for few hours \cite{23,31,35,37,38} but preparation of catalyst inks for electrochemical measurements often include ultrasonication, too \cite{23,31,35,37,38}. Hence, it is of great importance to study the influence of ultrasonication on the MOF structure and composition. XAS is a suitable method to ensure that the studied ink still contains the synthesized MOF(-derived) structure. It should be mentioned that using Nafion as a binder in the catalyst ink might influence the MOF catalyst performance. Nafion is often discussed to inhibit the electrical conductivity, block active sites of the catalyst layer and hence, decrease OER activity \cite{39}. However, Liu et al.
state that Nafion leads to a steric hindrance effect that enhances the catalytic activity of the analyzed carboxylic acid-based Co-MOFs. Growing MOFs directly on an electrically conducting substrate to analyze binder-free catalysts, as carried out by Cheng et al. [23], provides generally a favorable electrical conductivity and should be studied further.

Conclusion

In summary, MOF catalysts are affected by chemical transformations that lead to high OER activity. Operando XAS measurements lead to an understanding of the local structure–performance relations for the complex electrochemical processes occurring during the OER on an atomic and molecular level. Therefore, it is a useful technique to extract the internal driving force for the described transformations during OER and possible strategies for promoting this favorable transformation. However, the stability of the studied material under X-ray radiation and the focus on the local environment in XAS studies need to be considered. In addition, the pre-conditioning of the sample also needs to be taken into account when performing operando XAS, such as the previous cycling in the OER region or ultrasonicication of the electrodes. Operando x-ray diffraction measurements could complement XAS measurements by monitoring the overall MOF structure transformations during OER. Hence, further research perspectives include the combination of different operando techniques for a detailed analysis of the electronic and structural transformations occurring during OER to develop a concept for electrocatalysts with even better OER performances.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.coelec.2021.100845.
References

Papers of particular interest, published within the period of review, have been highlighted as:
* of special interest
** of outstanding interest

1. O’Malley MJ, Anwar MB, Heinen S, Kober T, McCalley J, McPherson M, Muratori M, Orths A, Ruth M, Schmidt TJ, Tuohey A: Multicarrier energy systems: shaping our energy future. Proc IEEE 2020, 108:1437–1456, https://doi.org/10.1109/jproc.2020.2902251.

2. Li Y, Wang W, Huang B, Mao Z, Wang R, He B, Gong Y, Wang H: Abundant heterointerfaces in MOF-derived hollow CoS2–MoS2 nanosheet array electrocatalysts for overall water splitting. J. Energy Chem. 2021, 57:99–108, https://doi.org/10.1016/j.jenergychem.2020.08.064.

3. Dong W, Zhou H, Mao B, Zhang Z, Liu Y, Liu Y, Li F, Zhang D, Zhang G, Shi W: Efficient MOF-derived V–Ni3S2 nanosheet arrays for electrocatalytic overall water splitting in alkaline. Int J Hydrogen Energy 2021, 46:10773–10782, https://doi.org/10.1016/j.ijhydene.2020.12.192.

4. Fabbi E, Habereder A, Walter K, Kötz R, Schmidt TJ: Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction. Catal. Sci Technol 2014, 4:3830–3821, https://doi.org/10.1039/c4cy00669k.

5. Beall CE, Fabbri E, Schmidt TJ: Peroxidative oxide-based electrodes for the oxygen reduction and evolution reactions: the underlying mechanism. ACS Catal 2021, 11:3034–3114, https://doi.org/10.1021/acscatal.0c004473.

6. Fabbi E, Schmidt TJ: Oxygen evolution reaction—the enigma in water electrolys. ACS Catal 2018, 8:9765–9774, https://doi.org/10.1021/acscatal.8b02712.

7. Lu XF, Fang Y, Luan D, Lou XWD: Metal–organic frameworks derived functional materials for electrochemical energy storage and conversion: a mini review. Nano Lett 2021, 21:1555–1565, https://doi.org/10.1021/acs.nanolett.0c08498.

8. Zhang B, Zheng Y, Ma T, Yang C, Peng Y, Zhou Z, Zhou M, Li S, Wang Y, Cheng C: Designing MOF nanoarchitectures for electrochemical water splitting. J Adv Mater 2021, 33, e2006042, https://doi.org/10.1002/adma.202006042.

9. Li Z, Gao R, Feng M, Deng YP, Xiao D, Zheng Y, Zhao Z, Luo D, Liu Y, Zhang Z, Wang D, Li Q, Li H, Wang X, Chen Z: Modulating metal–organic frameworks as advanced oxygen electrocatalysts. Adv Energy Mater 2021, 11, https://doi.org/10.1002/aenm.202003291.

10. Li S, Gao Y, Li N, Ge L, Bu X, Feng P: Transition metal-based bimetallic MOFs and MOF-derived catalysts for electrochemical oxygen evolution reaction. Energy Environ Sci 2021, 14:1897–1927, https://doi.org/10.1039/d0ee03697h.

11. Du J, Li F, Sun L: Metal-organic frameworks and their derivatives as electrocatalysts for the oxygen evolution reaction. Chem Soc Rev 2021, 50:2663–2695, https://doi.org/10.1039/d0cs01191f.

12. Wang HF, Chen L, Pang H, Kaskel S, Xu Q: MOF-derived electrocatalysts for oxygen reduction, oxygen evolution and hydrogen evolution reactions. Chem Soc Rev 2020, 49:1414–1448, https://doi.org/10.1039/c9cs00906j.

13. Moschkowitz Ch, Wonen S, Dhaka K, Zion N, Honig H, Tsaur Y, Caspary-Toroker M, Elbaz L: Bifunctional PGM-free metal organic framework-based electrocatalysts for alkaline electrolyzers: trends in the activity with different metal contents. Nanoscale 2021, 13:4576–4584, https://doi.org/10.1039/d0nr07875a.

14. Ranocchiar: Design of molecular heterogeneous catalysts with metal-organic frameworks. In Heterogeneous Catalysis: Advanced Design, Characterization and Applications. Wiley-VCH GmbH, 2021, https://doi.org/10.1002/9783527873599.ch8.

15. Wang X, Xia H, Li A, Li Z, Liu S, Zhang Q, Gong Y, Zheng L, Zhou Y, Chen C, Wang D, Peng Q, Gu L, Han X, Li J, Li Y: Constructing NiCoFe3S4 heteropolates within MOF-74 for efficient oxygen evolution reactions. J Am Chem Soc 2018, 140:15336–15341, https://doi.org/10.1021/jacs.8b08744.

16. Ahn W, Park MG, Lee DJ, Seo MH, Jiang G, Cao ZP, Hassan FM, Chen Z: Hollow multivacoid nanocuboids derived from ternary Ni-Co-Fe prussian blue analog for dual-electrocatalysis of oxygen and hydrogen evolution reactions. Adv Funct Mater 2018, 28, https://doi.org/10.1002/adfm.201902125.

17. Chen C, Tuo Y, Lu Q, Lu H, Zhang S, Zhou Y, Zhang J, Liu Z, Kang Z, Feng X, Chen D: Hierarchical trimetallic Co–Ni–Fe oxides derived from core-shell structured metal-organic frameworks for highly efficient oxygen evolution reaction. Appl Catal B: Environ 2021, 287:119953, https://doi.org/10.1016/j.apcatb.2021.119953.

18. Sadud GR, Parrer B, Patel P, Paul A, Chaudhari JC, Srivastava DN, Suresh E: Co@N-doped carbon nanoframe derived by simple pyrolysis of mixed-ligand MOF as an active and stable oxygen evolution electrocatalyst. Appl Surf Sci 2020, 529:147081, https://doi.org/10.1016/j.apsusc.2020.147081.

19. Li X, Yang X, Xue H, Fang H, Xu Q: Metal–organic frameworks as a platform for clean energy applications. J. Energy Chem. 2020, 2:100027, https://doi.org/10.1016/j.jenergychem.2020.100027.

20. Sun F, Wang G, Ding Y, Wang C, Yuan B, Lin Y: NiFe-based metal-organic framework nanosheets directly supported on nickel foam acting as robust electrodes for electrochemical oxygen evolution reaction. Adv Energy Mater 2018, 8:1800584, https://doi.org/10.1002/aenm.201800584.

21. Lee MK, Shokouhimehr M, Kim SY, Jiang HW: Two-dimensional metal–organic frameworks and covalent–organic nanoframe works for electrocatalysis: distinct merits by the reduced dimension. Adv Energy Mater 2021, 529:2003990, https://doi.org/10.1002/aenm.202003990.

22. Shrestha NK, Patil SA, Cho S, Jo Y, Kim H, Im H: Cu–Fe–NH2 based metal–organic framework nanosheets via drop-casting for highly efficient oxygen evolution catalysts durable at ultrahigh currents. J Mater Chem A 2020, 8:24408–24418, https://doi.org/10.1039/d0ta07716j.

23. Cheng C-C, Cheng P-Y, Huang C-L, Senthil Raja D, Wu Y-J, Lu S-Y: Gold nanocrystal decorated trimetallic metal organic frameworks as high performance electrocatalysts for oxygen evolution reaction. Adv Catal B Environ 2021, 286:119916, https://doi.org/10.1016/j.apcatb.2021.119916.

24. Fan L, Kang Z, Li M, Sun D: Recent progress in pristine MOF-based catalysts for electrochemical hydrogen evolution, oxygen evolution and oxygen reduction. Dalton Trans 2021, 50:5732–5753, https://doi.org/10.1039/d0dt00302j.

25. Gao J, Huang Q, Wu Y, Lan Y-Q, Chen B: Metal–organic frameworks for photo/electrocatalysis. Adv Energy Sustain Res 2021:2100033, https://doi.org/10.1002/aesr.202100033.

26. Liang Z, Gqi T, Gao S, Zhong R, Zou R: Multi-scale design of metal–organic framework-derived materials for energy electrocatalysis. Adv Energy Mater 2021:2003410, https://doi.org/10.1002/aenm.202003410.

27. Qi Q, Hu J, Zhang Y, Li W, Huang B, Zhang C: Two-dimensional metal–organic frameworks-based electrocatalysts for oxygen evolution and oxygen reduction reactions. Adv Energy Mater 2020, 2021:2000067, https://doi.org/10.1002/aenm.20200067.

28. Komienko N: Operando spectroscopy of nanoscopic metal-covalent organic framework electrocatalysts. Nanoscale 2021, 13:1507–1514, https://doi.org/10.1039/d0nr00768f.

29. Li C, Zhao J-W, Xie L-J, Wu J-Q, Ren Q, Wang Y, Li G-R: Carboxylate ligands-promoted superior electrocatalytic performance for oxygen evolution reaction and their mechanisms. 2021, https://doi.org/10.21203/rs.3.rs-154877/v1.
30. Liang J, Gao X, Guo B, Ding Y, Yan J, Guo Z, Tse ECM, Liu J: Ferrocene-based metal-organic nanofibrous catalysts for oxygen evolution reaction. Angew Chem Int Ed Engl 2021, 60, https://doi.org/10.1002/anie.202101878.

31. Zhao S, Wang Y, Dong J, He C-T, Yin H, An P, Zhao K, Zhang X, ** Gao C, Zhang L, Lv J, Wang J, Zhang J, Khattak AM, Khan NA, Wei Z, Zhang J, Liu S, Zhao H, Tang Z: Ultrathin metal–organic framework nanosheets for electrocatalytic oxygen evolution. Nat Energy 2016, 1, https://doi.org/10.1038/nenergy.2016.184.

This is the first study focusing on operando XAS characterization of MOFs in OER. The stability of the MOF under X-ray irradiation was determined to be sufficient. The improved OER performance of ultrathin NiCo-MOF nanosheets compared to pristine NiCo-MOF was related to a better adsorption of OER intermediates at the unsaturated metal sites. In addition, NiCo-coupling was suggested to increase OER performance.

32. Fabbri E, Abbott DF, Nachtegaal M, Schmidt TJ: Operando X-ray absorption spectroscopy: a powerful tool toward water splitting catalyst development. Curr Opin Electrochem 2017, 5: 20–26, https://doi.org/10.1016/j.coelec.2017.08.009.

33. Abbott DF, Lebedev D, Walter K, Povia M, Nachtegaal M, Fabbri E, Copéret C, Schmidt TJ: Iridium oxide for the oxygen evolution reaction: correlation between particle size, morphology, and the surface hydroxo layer from operando XAS. Chem Mater 2016, 28: 6591–6604, https://doi.org/10.1021/acs.chemmat.6b02625.

34. Kim BJ, Fabbri E, Abbott DF, Cheng X, Clark AH, Nachtegaal M, Borlaf M, Castelli IE, Graule T, Schmidt TJ: Functional role of Fe-doping in Co-based perovskite oxide catalysts for oxygen evolution reaction. J Am Chem Soc 2019, 141: 5231–5240, https://doi.org/10.1021/jacs.8b12101.

35. Zhao S, Tan C, He C-T, An P, Xie F, Jiang S, Zhu Y, Wu K-H, ** Zhang B, Li H, Zhang J, Chen Y, Liu S, Dong J, Tang Z: Structural transformation of highly active metal–organic framework electrocatalysts during the oxygen evolution reaction. Nat Energy 2020, 5: 881–890, https://doi.org/10.1038/s41560-020-00709-1.

Zhao et al. provide a detailed XAS study of the transformation of the Ni centers in NiO- and NiCo-MOF-74 catalysts during OER. The transformation of Ni into *OH and then *OOH analogues with increasing potential was discussed. In addition, it is suggested that Co and Fe enhance the Ni oxyhydroxide formation, which is most likely the key OER active species.

36. Abbott DF, Fabbri E, Borlaf M, Bozza F, Schäublin R, Nachtegaal M, Graule T, Schmidt TJ: Operando X-ray absorption investigations into the role of Fe in the electrochemical stability and oxygen evolution activity of Ni1-xFexOy nanoparticles. J Mater Chem A 2018, 6: 24534–24549, https://doi.org/10.1039/c8ta09336a.

37. Ji Q, Kong Y, Wang C, Tan H, Duan H, Hu W, Li G, Lu Y, Li N, ** Wang Y, Tian J, Qi Z, Sun Z, Hu F, Yan W: Lattice strain induced by linker scission in metal–organic framework nanosheets for oxygen evolution reaction. ACS Catal 2020, 10: 5691–5697, https://doi.org/10.1021/acscatal.0c00989.

Lattice strain was induced in NiFe-MOFs to enhance the OER activity. The improved OER performance was analyzed by operando XAS and ascribed to faster *OOH formation at the Ni sites due to a favorable electronic configuration, which is attributed to a partial electron transfer from Ni to Fe.

38. Zhao S, Zhang D, Jiang S, Cui Y, Li H, Dong J, Xie Z, Wang D-W, Amal R, Xia Z, Dai L: Carbon-supported layered double hydroxide nanodots for efficient oxygen evolution: active site identification and activity enhancement. Nano Res 2021, https://doi.org/10.1007/s12274-021-3358-3.

Layered double hydroxide nanodots supported on a MOF-derived carbon matrix were analyzed during OER using operando XAS. The authors suggest that the enhanced OER activity results from an increased number of active sites due to the high surface area of nanodots, an improved electron transfer and diffusion pathway through the MOF-derived porous carbon network and the Ni–Fe coupling effect.

39. Wang Z, Jiao S, Wang B, Kang Y, Yin W, Lv X, Zhang Q, Zhang Z, Chen Y, Pang G: In-situ growth of Fe–Co Prussian-blue-analog nanocages on Ni(OH)2/NF and the derivative electrocatalysts with hierarchical cage-on-sheet architectures for efficient water splitting. Int J Hydrogen Energy 2021, 46: 8345–8355, https://doi.org/10.1016/j.ijhydene.2020.12.045.

40. Liu M, Kong L, Wang X, He J, Zhang J, Zhu J, Bu X-H: Deciphering of advantageous electrocatalytic water oxidation behavior of metal-organic framework in alkaline media. Nano Res 2021, https://doi.org/10.1007/s12274-021-3404-1.

The influence of Nafion on the OER performance of MOFs based on carboxylic acid was analyzed using different (in-situ) methods. Hence, this is the first study discussing a positive influence of Nafion on the catalytic activity of these MOFs, due to a steric hindrance effect and an optimized electronic structure.