Observation of oxygen evolution over a \{Ni_{12}\}-cluster-based metal-organic framework

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The development of efficient electrocatalysts based on non-noble metals for oxygen evolution reaction (OER) remains an important and challenging task. Multinuclear transition-metal clusters with high structural stability are promising OER catalysts but their catalytic role is poorly understood. Here we report the crystallographic observation of OER activity over robust \{Ni_{12}\}-clusters immobilised in a porous metal-organic framework, NKU-100, by single-crystal X-ray diffraction as a function of external applied potential. We observed the aggregation of confined oxygen species around the \{Ni_{12}\}-cluster as a function of applied potential during the electrocatalytic process. The refined occupancy of these oxygen species shows a strong correlation with the variation of current density. This study demonstrates that the enrichment of oxygen species in the secondary coordination sphere of multinuclear transition-metal clusters can promote the OER activity.

metal-organic framework, oxygen evolution reaction, secondary coordination sphere, X-ray diffraction, binding site

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Oxygen evolution reaction (OER) plays a critical role in catalytic water splitting [1–3]. Over the recent past, rapid progress has been made in the study of catalytic performance and mechanism of various types of OER electrocatalytic systems. Non-noble metal-based electrocatalysts have been evaluated in OER, and cobalt, nickel, and iron compounds attracted much attention due to their high catalytic activities and earth abundance [4–6]. The OER mechanism has been investigated by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, scanning electrochemical microscopy (SEM), X-ray photoelectron spectroscopy (XPS), ultraviolet-visible (UV-vis) spectroscopy, differential electrochemical mass spectrometry, and Mössbauer spectroscopy, affording key insights into the design of efficient OER catalysts [7,8]. These spectroscopic techniques were employed to probe insights into the molecular details of the OER process. However, the observation of possible intermediates and their interactions with the active sites of electrocatalysts during the OER process at a crystallographic resolution has not been achieved to date.

Coordination compounds incorporating metal sites have shown promising activity for OER due to their abundant active sites and diverse binding modes to the reactants, but...
the aggregation of metal sites inevitably leads to the loss of catalytic activity [9]. For multinuclear coordination clusters, the ligands can promote the stabilisation of the atomically dispersed active sites, but the clusters often dissolve in electrolyte-containing strong acid or base, thus showing poor catalytic stability [10]. To address this problem, constraining the coordination cluster in framework materials, such as metal-organic frameworks (MOFs), is a promising strategy.

Porous MOFs, constructed by metal nodes and organic linkers, have been widely studied for gas storage and separation, sensing and catalysis [11–13]. MOFs have been used as electrocatalysts for OER, hydrogen evolution reaction, and CO\textsubscript{2} reduction reaction due to their highly tuneable structures with well-defined active sites [14–22]. There are two main advantages of the application of multinuclear clusters constrained in MOFs as electrocatalysts: (1) the framework structure affords high catalytic stability by hindering the aggregation of metal sites and dissolution in electrolyte; (2) the porous matrix boosts the reaction rate by increasing the concentration of the reactants around the atomically-dispersed active sites within the pores [23,24]. More importantly, the crystalline nature of MOFs could potentially enable the observation of dynamic reaction intermediates by advanced single-crystal X-ray diffraction (SCXRD), revealing fundamental insights into the OER activity. However, such a structural insight has been poorly established to date.

Herein, we reported the crystallographic study of the OER activity over \{Ni\textsubscript{12}\}-clusters confined in a highly stable MOF, [NH\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}]\textsubscript{3}\textsubscript{2}[Ni\textsubscript{3}(L)\textsubscript{1,4,5}(\mu\textsubscript{3}-O)(HCOO)(H\textsubscript{2}O)]·2H\textsubscript{2}O, (NKU-100, H\textsubscript{4}L = biphenyl-3,3′,5,5′-tetracarboxylic acid), which has triangle-shaped channels with the size of ~6.7 Å (Figure 1). NKU-100 crystallized in trigonal $P\bar{3}$ space group [25]. Each cluster is formed by an Ni\textsubscript{12}O\textsubscript{6} (Ni1) ring in the middle, which is sandwiched by two Ni\textsubscript{2}(HCOO)\textsubscript{3} (Ni2) triangles connected by six $\mu$-O atoms (Figure 1). It is noted that six Ni(II) sites of the \{Ni\textsubscript{12}\}-cluster are coordinated with water molecules, which can act as active sites for OER [22].

NKU-100 exhibits an overpotential of 342 mV at 10 mA cm\textsuperscript{-2} in 0.1 M KOH. The addition of KNO\textsubscript{3} in the electrolyte can further reduce the overpotential: in 0.1 M KOH with 1 M KNO\textsubscript{3}, the overpotential is 299 mV at 10 mA cm\textsuperscript{-2}, comparable with most MOF-based OER electrocatalysts under the same condition (Tables S1 and S2, Supporting Information online). The use of medium alkaline condition is beneficial to the stability of MOF-based electrocatalysts, and the subsequent linear sweep voltammetry (LSV) curves, chronopotentiometric curves, powder X-ray diffraction (PXRD) patterns, and N\textsubscript{2} adsorption isotherms demonstrate the high stability of NKU-100. Importantly, the molecular details of the OER processes over NKU-100 have been revealed by SCXRD, representing the first example of such studies of OER in MOFs. The occupancy of confined oxygen species inside the channel near the \{Ni\textsubscript{12}\}-clusters shows highly correlated changes with the applied potentials, demonstrating the key role of adsorption of oxygen species in the secondary coordination sphere of \{Ni\textsubscript{12}\}-clusters in promoting the OER activity (the first coordination sphere refers to guest molecules that are coordinatively bound to the cluster).

The stability of MOFs toward acid and base is crucial to their catalytic stability, which can be tuned by the modification of the electrolyte. In general, high concentrations of 1.0 M acid or base (or even higher) are beneficial for enhancing the OER, but such corrosive conditions are extremely detrimental to both the electrocatalysts and the reactors [26,27]. NKU-100 is stable in 0.1 M KOH and 0.001 M HCl (pH = 13 to 3) for at least 1 day as confirmed by PXRD measurements (Figure S1, Supporting Information online), placing NKU-100 as one of the most stable MOFs known to date (Table S3) [28,29]. In comparison with other cluster-based MOFs, NKU-100 shows very high stability (Table S4), originated from its 12-nuclear \{Ni\textsubscript{12}\} clusters that can effectively sustain the framework structure. To increase the conductivity at a relatively low concentration of base (0.1 to 0.01 M KOH), 1 M KNO\textsubscript{3} was used as additive to the

![Figure 1](image-url)  (a) The structure of ligand and metal centre; (b) three coordination layers in the cluster; (c) the framework with channels of NKU-100. Red for O, grey for C, green for Ni. For (b), orange, blue, rose are for Ni in the up, middle, down layers, respectively (color online).
electrolyte, in which NKU-100 is stable (Figure S1) and shows enhanced performance of OER (Figure 2). It has been reported that the addition of KNO₃ enhances the ionic strength (μ), which mitigates the diffuse double layer effects [30]. The role of potassium ions in the OER process has been described as a binder with reaction intermediates to lower the overpotentials. The acidity, size [31] and hydration enthalpies [32] can all influence the OER properties.

To optimise the OER performance, a series of experiments were performed by varying both the electrode materials and the electrolyte. Firstly, the ratio of NKU-100/carbon black (simplified to C in the following description) (Figure S2) and loading of NKU-100 on the glass carbon electrode for the OER performance have been optimised (Figure S3). A loading of 2 mg cm⁻² with an MOF/C ratio of 1:1 (m/m) shows the best OER performance with an overpotential at 342 mV in 0.1 M KOH. Secondly, the impacts of the electrolyte, base, potassium salts, and concentration of KNO₃ on the OER performance have been studied. KOH shows better performance than NaOH and LiOH (Figure S4). To determine the suitable potassium salt, various common potassium salts (0.5 M) were tested in 0.1 M KOH. The change of pH upon adding of potassium salts is within 0.02 as measured by a pH meter. K₂CO₃, KNO₃, and K₂SO₄ show better performance in the OER than KCF₃SO₃ and K(CH₃COO) (Figure S5), with overpotentials at 308, 328, 327, 348, and 350 mV, respectively, and KNO₃ was chosen based upon its great solubilities. The OER performance of NKU-100 increases with the increased concentration of KNO₃ from 0 to 1 M in the electrolyte, but little change is observed on further increase of the concentration of KNO₃ to 3 M (Figure S6).

LSV curves show that for the OER test in 0.1 M KOH electrolyte, the overpotentials decrease from 342 to 299 mV with 1 M KNO₃ (Figure 2a). Parallel experiments using different batches of NKU-100 have been performed to validate the observation (Figure S7). The overpotentials of NKU-100 are lower than that of commercial electrocatalyst RuO₂ (1,212 and 352 mV in 0.01 and 0.1 M KOH, respectively, Figure S8). The corresponding Tafel slopes for NKU-100 in 0.01 and 0.1 M KOH also decrease significantly from 1,273/279 to 345/220 mV dec⁻¹ with the addition of KNO₃ (Figure 2b), demonstrating the enhanced kinetics of OER with KNO₃ by mitigating the diffuse double layer effects [30]. The electrochemical active surface area (ECSA) was evaluated by electrochemical double-layer capacitance (Cdl) [18,33,34]. Cyclic voltammetry (CV) measurements were performed between 0.2 and 0.3 V (vs. Ag/AgCl) at the rates of 70–180 mV s⁻¹ (Figure S9). As shown in Figure 2c, the Cdl of NKU-100 in 0.01 M KOH and 0.1 M KOH are both smaller than that in 1 M KNO₃, indicating that the addition of KNO₃ to the electrolyte increases the ECSA. With the addition of KNO₃, the ionic strength of the electrolyte increases. The increased number of free ions increases their contact with the catalytic active sites, resulting in an increase in ECSA. The gaseous product was collected and analyzed by gas chromatography, which confirms the main product of O₂ with a Faraday efficiency of ~98%. The product of O₂ is further confirmed by the rotating ring-disk electrode technique with a ~97% Faraday efficiency for O₂ (Figures S10 and S11) [35].

Figure 2 (a) LSV curves; (b) Tafel plots; (c) Cdl; (d) EIS of NKU-100 in different electrolytes; (e) chronopotentiometric curves at 10 mA cm⁻² in 0.1 M KOH; (f) N₂ isotherms at 77 K of NKU-100, carbon black, 1:1 (m/m) mixture of NKU-100 and carbon black, and the same mixture after 1,000-cycles of the OER test (color online).
To study the kinetics of the electrode reaction, the electrochemical impedance spectroscopy (EIS) was measured [36,37]. The equivalent circuit models are shown in Figure S12. The results indicate that NKU-100 in KOH with KNO₃ has higher ability of electron transfer than that without KNO₃ (Figure 2d). The plots of turnover frequency (TOF) vs. potential are shown in Figure S13a. In 0.01 M KOH, TOF value increases from 0.00125 to 0.00275 s⁻¹ upon addition of 1 M KNO₃, while in 0.1 M KOH, the value increases from 0.00313 to 0.00478 s⁻¹ (Figure S13b). Overall, the enhanced OER performance upon the addition of KNO₃ suggests that the extra ionic concentration of the electrolyte can increase the electronic transmission rate in the electrolyte without the use of high-concentration alkali because the rate of electron transport is also accelerated in this way.

To study the catalytic stability, LSV, chronopotentiometric curve, and multi-current process were measured. As shown in Figure S14, the subsequent LSV curves exhibit little difference compared with the initial curve after 1,000 cycles in 0.01 M KOH and 0.1 M KOH with or without KNO₃. The chronopotentiometric curves showed little change over 10,000 s in all tests (Figure 2e and Figure S15). These results demonstrate the high catalytic stability of NKU-100 during the OER process. Figure S16 shows a typical chronopotentiometric curve of NKU-100 upon the increase of current from 10 to 40 mA cm⁻² with an increment of ~3.3 mA cm⁻² per 500 s, indicating the high conductivity, mass transportation, and mechanical robustness of NKU-100 [23]. Furthermore, the analyses by PXRD (Figure S17), IR spectra (Figure S18), UV-vis spectra (Figure S19), ¹H nuclear magnetic resonance (¹H NMR) spectra (Figure S20), XPS (Figure S21), and N₂ isotherms at 77 K (Figure 2f and Figure S22) of the mixture of NKU-100 with carbon and that after 1,000 cycles of OER, and ¹H NMR of different electrolytes after 1,000 cycles of the reaction (Figure S23) unambiguously confirm that NKU-100 is a highly stable electrocatalyst for OER. Additionally, analyses of the IR spectra and in situ Raman spectra of NKU-100 as a function of applied potentials further confirm its high stability (Figures S24 and S25).

Single crystal diffraction data were collected for NKU-100 as a function of applied potential under reaction conditions to determine the active sites for OER. An equilibrium time of 0.5 h was taken at each potential before data collection. Compared with the structure determined in the absence of an external potential, upon applying the potential, two distinct oxygen sites, denoted as O1 and O2 are observed around the \( \{ \text{Ni}_{12} \} \)-cluster (Figure 3a). O1 and O2 are located 3.016/2.997 Å (blue dotted line) from a coordinated carboxylate oxygen atom, 3.001/3.008 Å (orange dotted line) from another carboxylate oxygen atom, and 3.240/3.230 Å (purple dotted line) from the \( \mu_3\)-O center, indicating the formation of moderate-to-strong host-guest hydrogen bonds.
between these oxygen sites. The distances between O1/O2 and the nearest Ni1 center are 3.715/3.705 Å (green dotted line). Fixing the occupancies of both sites be 0.5, the temperature factors of O1 and O2 both decrease from ~0.4 without applied voltage to ~0.1 Å² at 10 mA cm⁻² from difference Fourier analysis. To further confirm the crystallographically-determined binding sites by SCXRD, density functional theory (DFT) calculations for potential sites of the adsorption of water in the channels of NKU-100 have been calculated by the Monte Carlo method with the Adsorption Locator Tools in Material Studio [41]. As shown in Figure 3b along c axis, the calculation suggests that oxygen species are adsorbed at locations near the [Ni₁₂]ₘ cluster, highly consistent with the SCXRD results. As shown in Figure 3c, with the same thermal vibrational factors, increased potentials lead to increased occupancies of O1 and O2 because the increased electron transmission induces the attraction of additional oxygen atoms as electron donor (Tables S5 and S6) [42,43]. Interestingly, the trend of site occupancy shows an excellent agreement with the CV plots. The result confirms that the [Ni₁₂]ₘ clusters along with the channels are beneficial for the enrichment of the active oxygen species for enhanced OER performance under electric field [44,45]. In comparison with other MOF-based OER electrocatalysts, NKU-100 not only is stable owing to its multi-nuclear cluster-based framework (in 0.1 M KOH), but also has the channels with appropriate size (6.7 Å) to accommodate and enrich the catalytic reactants and intermediates to accelerate the reaction. With the aid of the second coordination sphere [35,46,47], oxygen species are bound tightly and thus activated efficiently in the channel via host-guest hydrogen bonds.

In conclusion, a highly robust MOF, NKU-100, incorporating 12-nuclear Ni-clusters, has shown excellent OER performance and long-term catalytic stability under medium alkaline conditions. SCXRD studies of NKU-100 as a function of applied potentials suggest that the OER occurred around the [Ni₁₂]ₘ cluster with intermediates stabilized in a hydrogen-bonding network. This work demonstrates that the second coordination sphere created by the multinuclear metal centers significantly influences the OER process, providing insights into the design of new efficient porous electrocatalysts.

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1. Jiao Y, Zheng Y, Jaroniec M, Qiao SZ. Chem Soc Rev, 2015, 44: 2060–2086
2. Suen NT, Hung SF, Quan Z, Zhang N, Xu YJ, Chen HM. Chem Soc Rev, 2017, 46: 337–365
3. Yang H, Gao S, Rao D, Zhang C, Zhou X, Yang S, Ye J, Yang S, Lai F, Yan X. Sci China Chem, 2021, 64: 101–108
4. Li W, Li F, Zhao Y, Li C, Li Y, Yang H, Fan K, Zhang P, Shan Y, Sun L. Sci China Chem, 2022, 65: 382–390
5. He J, Zou Y, Huang Y, Li C, Liu Y, Zhou L, Dong CL, Lu X, Wang S. Sci China Chem, 2020, 63: 1684–1693
6. Yan D, Li Y, Hoo J, Chen R, Dai L, Wang S. Adv Mater, 2017, 29: 1606459
7. Zhu K, Zhu X, Wang Y. Angew Chem Int Ed, 2019, 58: 1252–1265
8. Yuan W, Zhu B, Li XY, Hansen TW, Ou Y, Fang K, Yang H, Zhang Z, Wagner JB, Gao Y, Wang Y. Science, 2020, 367: 428–430
9. Yuan S, Chen YP, Qin J, Lu W, Wang X, Zhang Q, Bosch M, Liu TF, Lian X, Zhou HC. Angew Chem Int Ed, 2015, 54: 14696–14700
10. Zhang Q, Guan J. ChemSusChem, 2019, 12: 3209–3235
11. Zhou HC, Long JR, Yaghi OM. Chem Rev, 2012, 112: 673–674
12. Batten SR, Champness NR, Chen XM, Garcia-Martinez J, Kitagawa S, Øhrstrøm L, O’Keefe M, Paik Suh M, Reijndijk J. Pure Appl Chem, 2013, 85: 1715–1724
13. Zhu L, Liu XQ, Jiang HL, Sun LB. Chem Rev, 2017, 117: 8129–8176
14. Kornienko N, Zhao Y, Kley CS, Zhu C, Kim D, Lin S, Chang CJ, Yaghi OM, Yang P. J Am Chem Soc, 2015, 137: 14129–14135
15. Mann P, Deb Gupta J, Bose S, Das SK. Angew Chem Int Ed, 2016, 55: 2425–2430
16. Wang YR, Huang Q, He CT, Chen Y, Liu J, Shen FC, Lan YQ. Nat Commun, 2018, 9: 4466
17. Wang S, Gao X, Hang X, Zhu X, Han H, Li X, Liao W, Chen W. Nat Chem, 2018, 140: 6271–6277
18. Wang XL, Dong LZ, Qiao M, Tang YJ, Liu J, Li Y, Li SL, Su JX, Lan YQ. Angew Chem Int Ed, 2018, 57: 9660–9664
19. Huang J, Li Y, Huang RK, He CT, Gong L, Hu Q, Wang L, Xu YT, Tian XY, Liu SY, Ye ZM, Wang F, Zhou DD, Zhang WX, Zhang JP. Angew Chem, 2018, 130: 4722–4726
20. Xu YT, Ye ZM, Ye JW, Cao LM, Huang RK, Wu JX, Zhou DD, Zhang XF, He CT, Zhang JP, Chen XM. Angew Chem Int Ed, 2019, 58: 139–143
21. Zhou W, Huang DD, Wu YP, Zhao J, Wu T, Zhang J, Li DS, Sun C, Feng P, Bu X. Angew Chem Int Ed, 2019, 58: 4227–4231
22. Zhao S, Tan C, He CT, An P, Xie F, Jiang S, Zhu Y, Wu KH, Zhang B, Li H, Zhang J, Chen Y, Liu S, Dong J, Tang Z. Nat Energy, 2020, 5: 881–890
23. Kung CW, Mondloch JE, Wang TC, Bury W, Hoffeditz W, Klahr BM, Klet RC, Pellin MJ, Farha OK, Hupp JT. ACS Appl Mater Interfaces, 2015, 7: 28223–28230
24 Tao L, Lin CY, Dou S, Feng S, Chen D, Liu D, Huo J, Xia Z, Wang S. *Nano Energy*, 2017, 41: 417–425
25 Han Z, Li J, Lu W, Wang K, Chen Y, Lin L, Zhang X, Han X, Teat SJ, Frogley MD, Yang S, Shi W, Cheng P. *Angew Chem Int Ed*, 2022, 61: e202115585
26 Guan C, Liu X, Ren W, Li X, Cheng C, Wang J. *Adv Energy Mater*, 2017, 7: 1602391
27 Garcés-Pineda FA, Blasco-Ahicart M, Nieto-Castro D, López N, Galán-Mascarós JR. *Nat Energy*, 2019, 4: 519–525
28 Brown ID. *Chem Rev*, 2009, 109: 6858–6919
29 Howarth AJ, Liu Y, Li P, Li Z, Wang TC, Hupp JT, Farha OK. *Nat Rev Mater*, 2016, 1: 15018
30 Huynh M, Bediako DK, Nocera DG. *J Am Chem Soc*, 2014, 136: 6002–6010
31 Zaffran J, Stevens MB, Trang CDM, Nagli M, Shehadeh M, Boettcher SW, Caspary Toroker M. *Chem Mater*, 2017, 29: 4761–4767
32 Kuznetsov DA, Konev DV, Sokolov SA, Fedyanin IV. *Chem Eur J*, 2018, 24: 13890–13896
33 He P, Yu XY, Lou XWD. *Angew Chem Int Ed*, 2017, 56: 3897–3900
34 Hu F, Zhu S, Chen S, Li Y, Ma L, Wu T, Zhang Y, Wang C, Liu C, Yang X, Song L, Yang X, Xiong Y. *Adv Mater*, 2017, 29: 1606570
35 Li Q, Lu L, Liu J, Shi W, Cheng P. *J Energy Chem*, 2021, 63: 230–238
36 Kuang M, Zhang J, Liu D, Tan H, Dinh KN, Yang L, Ren H, Huang W, Fang W, Yao J, Hao X, Xu J, Liu C, Song L, Liu B, Yan Q. *Adv Energy Mater*, 2020, 10: 2002215
37 Huang W, Zhang J, Liu D, Xu W, Wang Y, Yao J, Tan HT, Dinh KN, Wu C, Kuang M, Fang W, Dangol R, Song L, Zhou K, Liu C, Xu JW, Liu B, Yan Q. *ACS Nano*, 2020, 14: 17640–17651
38 Zhao S, Wang Y, Dong J, He CT, 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. *Nat Energy*, 2016, 1: 16184
39 Rui K, Zhao G, Chen Y, Lin Y, Zhou Q, Chen J, Zhu J, Sun W, Huang W, Dou SX. *Adv Funct Mater*, 2018, 28: 1801554
40 Xing J, Guo K, Zou Z, Cai M, Du J, Xu C. *Chem Commun*, 2018, 54: 7046–7049
41 Zhang M, Wang W, Chen Y. *Phys Chem Chem Phys*, 2018, 20: 2211–2219
42 Görlin M, de Araújo JF, Schmies H, Bernsmeier D, Dresp S, Gieleich M, Jusys Z, Chernev P, Kraehnert R, Dau H, Strasser P. *J Am Chem Soc*, 2017, 139: 2070–2082
43 Grimaud A, Diaz-Morales O, Han B, Hong WT, Lee YL, Giordano L, Störzinger KA, Koper MTM, Shao-Horn Y. *Nat Chem*, 2017, 9: 457–465
44 Ni Z, Jerrell JP, Cadwallader KR, Masel RI. *Anal Chem*, 2007, 79: 1290–1293
45 Gu ZY, Wang G, Yan XP. *Anal Chem*, 2010, 82: 1365–1370
46 Leenders SHAM, Gramage-Doria R, de Bruin B, Reek JNH. *Chem Soc Rev*, 2015, 44: 433–448
47 Trouvé J, Gramage-Doria R. *Chem Soc Rev*, 2021, 50: 3565–3584