In Silico Design of Covalent Organic Framework-Based Electrocatalysts

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ABSTRACT: Covalent organic frameworks (COFs) are an emerging type of porous crystalline material for efficient catalysis of the oxygen evolution reaction (OER). However, it remains a grand challenge to address the best candidates from thousands of possible COFs. Here, we report a methodology for the design of the best candidate screened from 100 virtual M−N_xO_y (M = 3d transition metal)-based model catalysts via density functional theory (DFT) and machine learning (ML). The intrinsic descriptors of OER activity of M−N_xO_y were addressed by the machine learning and used for predicting the best structure with OER performances. One of the predicted structures with a Ni−N_2O_2 unit is subsequently employed to synthesize the corresponding Ni−COF. X-ray absorption spectra characterizations, including XANES and EXAFS, validate the successful synthesis of the Ni−COF coordination environment. The studies of electrocatalytic activities confirm that Ni−COF is comparable with the best reported COF-based OER catalysts. The current density reaches 10 mA cm⁻² at a low overpotential of 335 mV. Furthermore, Ni−COF is stable for over 65 h during electrochemical testing. This work provides an accelerating strategy for the design of new porous crystalline-material-based electrocatalysts.

KEYWORDS: oxygen evolution reaction, machine learning, intrinsic descriptors, covalent organic frameworks, DFT calculations, Ni−N_2O_2 coordination

INTRODUCTION

Exploring highly active electrocatalysts for the oxygen evolution reaction (OER) is key to water splitting and metal−air batteries. Because the OER has a four-electron transfer process, it often suffers from a high overpotential to overcome its kinetic barrier. 1−3 Numerous novel electrocatalysts have been developed to improve OER activity. Because of the high surface area, highly periodic structural units, and abundant coordination of unsaturated metal sites, many porous crystalline materials, such as metal organic frameworks (MOFs) and covalent organic frameworks (COFs), have shown high potential in electrocatalytic oxygen evolution activity. The demand for excellent OER electrocatalysts drives the rational structural design of porous crystalline materials to improve their electrocatalytic performance. 4−10

The local structural and metal-coordinated environment of active centers plays an important role in catalytic activity and stability. 11−14 Recently, single-atom catalysts based on typical transition metals, including Fe, Co, Ni, and Cu, have been regarded as promising candidates for electrocatalysis because of their well-defined single atomic site and tunable coordination environment. 15−17 For example, Duan’s group reported a general approach to a series of atomic 3d metals embedded in nitrogen-doped porous graphene frameworks with MN_C_4 moieties (M = Fe, Co, or Ni). The obtained Ni-NHGFSs had outstanding OER electrocatalytic activity. Because of the introduction of MN_C_4 moieties, porphyrin-based COFs have exhibited excellent electrocatalytic activity. Yaghi’s group incorporated porphyrin units within COFs and thus boosted their catalytic activity and selectivity toward carbon dioxide reduction. 18 Salen (N,N'-bis(salicyldiene)-ethylenediamine)-based covalent organic frameworks with COF backbones and functional Salen units could be a useful model to explore structure-performance relationships for high-activity electrocatalyst design. Various Salen-based COFs have been used as platforms for catalytic applications, such as asymmetric catalysis, catalytic antioxidants, and cycloaddition reactions. 20−23 For example, Wang’s group reported the first example of Salen-based COFs and explored the catalytic activity of the Henry reaction. 24 Cui’s group has also reported
Salen-derived chiral covalent organic frameworks that exhibited superior chemical stability for several asymmetric transformations.20 Salen-based COFs have demonstrated high crystallinity and chemical stability, which is beneficial to efficient catalytic reactions. Moreover, the metal active center, namely, Salen and Salen-derived complexes (Figure 1a), have a similar metal-coordinated environment to porphyrin, which makes Salen-based COFs demonstrate high catalytic activity. Many studies have been dedicated to regulating the coordination environment around the metal center. However, trial-and-error methodologies are still a time-consuming and laborious task. Therefore, computational material design combined with the ML algorithm is usually used to accelerate the design of COFs or other porous materials.25,26

In this work, various coordination units M−NₓOᵧ (M = 3d transition metal), with similar geometry to Salen, were first designed and screened. The DFT method was applied to simulate the free energy of the associative four-electron pathways toward the OER. A regression by machine learning (ML), based on DFT calculations, was performed to reveal the intrinsic descriptors that governed the activity of the simplified model catalysts. The ML method is commonly used in accelerating the prediction of the overpotential of oxygen evolution reactions.27,28 DFT calculations showed that Fe−NₓOᵧ (M = Zn, Fe, Co, Cu) possessed higher OER performances than other metal-based M−COFs (M = Zn, Fe, Co, Cu).

**RESULTS AND DISCUSSION**

**Calculated Electrocatalytic OER Activity**

Figure 1a presents the geometric structure of the simplified model catalyst M−NₓOᵧ adopted in this work. In the M−NₓOᵧ moiety, M is bonded with x N and y O atoms. Here, 10 3d transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) were chosen to construct Salen and Salen-derived structures. As NₓOᵧ has 10 possible combinations (O4,N O3,N O3-1, N2O2,N 2O2-1, N2O2-2, N2O2-3, N3O, N3O-1, and N4, more details can be found in Figures S1 and S3−S12), a total of 100 simplified model catalysts were considered in this work. After clarifying the structural properties of M−NₓOᵧ, we conducted DFT computations to evaluate the catalytic performance of these catalysts. The free energy diagram for the 100 simplified model catalysts was calculated, and the OER catalytic performance could be quantified by the theoretical potential of the rate-determining step. The DFT computational details and results are provided in the Supporting Information Section S4.
Adsorption–Activity Relationships

The free energy diagram for the ideal OER catalyst from the different simplified model catalysts is shown in Figures S3–S12. The free energy of the four associated electron pathways is determined by the adsorption free energies of the reaction intermediates *OH, *O, and *OOH. As shown in Figure 1b, we investigated the relationship between the adsorption free energies of the reaction intermediates and found that there was a strong linear relationship between \( \Delta G_{*\text{OH}} \) and \( \Delta G_{*\text{OOH}} \)

\[
\Delta G_{*\text{OOH}} = 0.89 \Delta G_{*\text{OH}} + 3.33
\]

The slope and intercept of the linear relationship were very similar to those calculated with the metal or metal oxide surface. According to the relationship between \( \Delta G_{*\text{OH}} \) and \( \Delta G_{*\text{OOH}} \), \( \Delta G_{*\text{OOH}} \) could be considered an independent variable to describe the \( U^\text{onset} \) for the OER with the simplified model catalysts. Plotting \( \eta_{\text{theory}} \) as a function of \( \Delta G_{*\text{OH}} - \Delta G_{*\text{OH}} \) for the simplified model catalysts led to a universal volcano relationship independent of the catalyst material (Figure 1c). As shown in Table S1, the potential-determining step can be either the formation of *OH, *O, or *OOH and the generation of O₂. The right branch of the volcano plot is piecewise linear in Figure 1c, indicating that the formation of *O is the determining step for these systems. The OER activity is enhanced with weaker *O adsorption. When \( \Delta G_{*\text{OH}} - \Delta G_{*\text{OH}} \) is less than 1.6 eV, \( \eta_{\text{theory}} \) is in the left branch of the volcano plot, and the formation of *OH or *OOH is the determining step, revealing that weaker *OH may enhance the OER performance.

Intrinsic Descriptor from Machine Learning

Although the adsorption free energies of *O and *OH exhibit a high correlation with the OER activity, the intrinsic characteristics of the active center that dominates the adsorbate binding strength are uncertain. In addition, the descriptors of \( \Delta G_{*\text{OH}} \) and \( \Delta G_{*\text{OH}} \) are unrealistic to experimentally measure and are highly expensive to calculate. Therefore, it is important to find intrinsic descriptors that are readily accessible in the database laboratory to describe the OER activity of the simplified model catalysts. With the advantage of machine learning in discovering the data correlation between chemical and material properties, a data set of 100 structures and 23 initial features (the total features are summarized in Table S2), such as the ionic radii, electronegativity, electron affinity, and first ionization energy of the metal, is built. The gradient boosting regression (GBR) algorithm has been used to evaluate the initial features to understand the relationship between features and the relationship between features and the target property \( \Delta G_{*\text{OH}} - \Delta G_{*\text{OH}} \). We used the Pearson correlation coefficient matrix to explore the data correlation between 23 initial features. The GBR algorithm has been used to sort feature importance. As shown in Figure S2a, Pearson correlation coefficient matrices were calculated to identify the correlations between the chosen optimal features. The importance of features sorted by the GBR algorithm is shown in Figure S2b. The average charge \( (q_{\text{ave}}) \) plays the most important role in \( \Delta G_{*\text{OH}} - \Delta G_{*\text{OH}} \) indicating that the electronic properties of the elements play the most important role in determining the adsorption properties of \( \Delta G_{*\text{OH}} - \Delta G_{*\text{OH}} \). To find the best feature set, first, we chose the 12 most important features. The features with a correlation greater than 0.5 and a lower importance score were then removed. Finally, four features were selected as an optimal feature set.

The optimal feature set contains structural features (bond length and ionic radius) and elemental properties (electron affinity and Mulliken charge). The definitions of the four features are shown in Figure 1d. For example, \( d_3 \) is the bond length between the metal ion and atom 2, while \( q_{\text{ave}} \) is the average charge of the active site. The active sites include atoms 1, 2, 3, and 4; the metal ions; and atom x. Atom x is used to simulate metal ions in different valence states. \( E_{\text{diff}} \) is the first electron affinity for the metal center. Furthermore, \( r_{\text{ins}} \) is the ionic radius of the active site atom. The atomic properties of saturation sites 1 and 2 are different from the properties of unsaturation sites 3 and 4. A more detailed definition of information can be found in Table S2. According to the feature importance analysis (Figure 1e), the electrical property, average charge, is the most important factor. The average charge of the active site directly determines the electrostatic interaction between intermediates and active site and affects the adsorption energy of intermediates. This result may demonstrate that the electrostatic interaction is the main component of the interaction between the active center and intermediates. The bond length and ionic radius of active site atoms determine the configuration of the active center, which may affect the combination between the intermediates and active center through steric hindrance. The fourth optimal feature, electron affinity, is a feature related to both size and electronic properties, and it is affected by atomic size and nuclear charge. Therefore, it may affect the adsorption energy of the intermediate in terms of space or electrical properties. In this work, we employ GBR regression algorithms to build the machine learning model. We performed 10-fold cross-validation instead of randomly splitting the data into one training and one test set. This method provides better estimates of the “out-of-sample” error than randomly train/test splitting for small data set training. We use the coefficient of determination \( (R^2) \) and root-mean-square error (RMSE) to evaluate the performance of the ML model. Figure 1f shows that the data trained with the GBR algorithm very closely straddles the perfect correlation line. The RMSE is 0.08, and the coefficient of determination is 0.994. The subplot clearly shows that the training/test set deviance decreases gradually with an increase in the boosting iteration numbers. Then, plotting \( \eta_{\text{theory}} \) as a function of the predicted \( \Delta G_{*\text{OH}} - \Delta G_{*\text{OH}} \) leads to a universal volcano relationship. This result indicates that ML methodologies can be implemented in the catalyst design pipeline to automatically discover and rank the importance of elemental property descriptors for the OER.

Preparation of M–COFs (M = Zn, Fe, Co, Ni, Cu)

From the free energy diagram calculation, we found that the 11 best performing metals with overpotentials smaller than 0.6 eV were Fe–N₅O₁, Co–N₅O₂-2, Sc–N₅O₃, Fe–N₅O₂, Co–N₅O₂, Ni–N₅O₁, Ni–O₅, Ni–N₅O₁-2, Fe–N₅O₂, and Cu–N₅O₂-1. We further incorporated the Fe–N₅O₂, Co–N₅O₂, and Ni–N₅O₂ moieties into COFs to prepare COF-based electrocatalysts for evaluating the DFT predictions of OER performance. Fe–N₅O₂, Co–N₅O₂, and Ni–N₅O₂ moieties are introduced into the COF structure as a linear connecting unit also as the main active center. According to previous electrochemical tests, the stability of 2D COFs is worse than 3D COFs. In addition, 3D COF can expose more metal active sites. Thus, we use THPM ligand and linear
connect $\text{M-N}_2\text{O}_2$ to construct the 3D Salen–COF structure. M–COFs ($\text{M} = \text{Zn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$) were synthesized via a Schiff-base condensation reaction of the corresponding metal acetate and ethylenediamine (EDA) with the ligand (THPM) in a solvothermal method (Figure 2a, for more details, see the Supporting Information). To analyze the covalent construction of COFs, we confirmed M–COFs by Fourier transform infrared (FT-IR) spectroscopy (Figure S13) and $^{13}\text{C}$ cross-polarization magic-angle spinning (CP/MAS NMR, Figure S14). As shown in Figure S13, the apparent peak at 1621 cm$^{-1}$ exhibits the formation of $\text{C}=\text{N}$ stretching bands and the disappearance of aldehyde groups. According to the solid-state $^{13}\text{C}$ CP/MAS NMR spectra of Zn–COF, the characteristic resonance peaks of imine carbons at 166 ppm are also observed. Transmission electron microscopy (TEM) images demonstrate that most of the M–COFs show a block-like morphology, although some show a sphere-like morphology (Figures 2 and Figure S15). Moreover, their energy-dispersive spectroscopy (EDS) mappings show that the distribution of metal elements is more uniform, which provides a guarantee for the subsequent electrocatalytic performance. According to the inductively coupled plasma (ICP) emission spectrometry results, the metal contents of M–COF ($\text{M} = \text{Zn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$) are 4.2, 6.6, 4.1, 5.6, and 8.1 wt %, respectively.

To further confirm the crystallinity of the resulting covalent frameworks, we conducted powder X-ray diffraction (PXRD) with the M–COFs. As shown in Figure 2c, d. All samples exhibit strong diffraction peaks in their XRD patterns and no residual peaks characteristic of the ligands, indicating that the resulting covalent frameworks have high crystallinity with a 3-fold interpenetration dia topology (Figure 2b). Moreover, the obtained Zn–COF shows good stability in different organic solvents, such as 1,4-dioxane, acetone, THF, CH$_2$Cl$_2$, mesitylene, EtOH, DMF, and H$_2$O (Figure S16). Thermogravimetric analysis (TGA) of the M–COFs was performed in a N$_2$ atmosphere. As shown in Figure S17, the TGA curves reveal that the M–COFs ($\text{M} = \text{Zn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$) are stable up to at least 200 °C. Nitrogen sorption isotherms were measured at 77 K to explore the porosity of the M–COFs ($\text{M} = \text{Zn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$). As shown in Figure S18, the nitrogen sorption isotherms display an increase below $P/P_0 < 0.05$, and they all show typical type I isotherms, revealing their microporous characteristics. The Brunauer–Emmett–Teller (BET) surface area was obtained by the $0.05 < P/P_0 < 0.30$ range of their isotherms. The BET surface areas are 642, 542, 636, 514, and 566 m$^2$ g$^{-1}$ for the M–COFs ($\text{M} = \text{Zn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$). According to Table S3, Ni–COF shows the highest total pore volume, which may benefit mass transport during the OER process.

To explore the metal-coordination environment and electronic structure of the best OER electrocatalyst (Ni–COF), we performed X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analysis of Ni–COF. From the XANES analysis (Figure 3a), the pre-edge of the sample shifts toward low energy by $\sim$0.5 eV compared to standard NiO, and the arising
edge of the main adsorption peak (≈8340 eV) of Ni−COF shifts toward low energy compared to NiO, suggesting the positive charge state of Ni in Ni−COF. In the survey spectrum of Ni−COF (Figure S21), apparent peaks appear at 285, 400, 532, and 855 eV, which could be assigned to C 1s, N 1s, O 1s, and Ni 2p regions. The C 1s spectrum was further fitted into two components, corresponding to −C−C/−C==C at 284.7 eV and −C−N/−C−O at 287.4 eV. In the following N 1s spectrum, apparent graphitic nitrogen region appeared at 401.1 eV and N−Ni region at 399.5 eV. In the O 1s spectrum, Ni−COF exhibits two regions, which can be assigned to Ni−O at 531.8 eV and −C−N/−C−O at 532.4 eV. The Ni 2p XPS spectrum of Ni−COF shows characteristic peaks at 869.9 and 852.7 eV, which can be assigned to Ni 2p 1/2 and Ni 2p 3/2 signals, respectively (Figure S21). The XPS results are also consistent with Ni2+ in a Ni−N2O2 coordination environment and the Ni K-edge XAS conclusions. According to the Fourier transform (FT) EXAFS of Ni−COF shown in Figure 3b, Ni−COF exhibits one main peak at 1.56 Å, which can be assigned to the coordination bonds of Ni−N or Ni−O. Clearly, no obvious peaks appearing at approximately 2.5–3 Å in the FT-EXAFS spectrum are observed, revealing the absence of Ni−Ni bonds in Ni−COF. As shown in Figures 3c, d and Figure S20, the corresponding EXAFS fitting curves of Ni−COF in the K-space and R-space show that the Ni atom is coordinated with two N atoms and two O atoms in the Ni−COF sample (detailed fitting parameters are shown in Table S4). Additionally, because of the small difference between the bond lengths of Ni−N and Ni−O, NiO is fitted. The fitting results show that the Ni−O bond length is 1.98 Å, whereas the Ni−O bond length is shortened because of the low coordination number of the Ni−COF sample, which is consistent with the fitting result. Wavelet transform (WT) was used to further confirm the coordination forms of Ni−N2O2 in the samples. In Figure 3e, the WT maximum at 7.5 Å−1 (x-axis: 2 Å) for Ni foil can be assigned to the Ni−Ni bonds. Moreover, a red-like position can be seen in NiO. Ni−O bonds exist in the orange-red position where the x-axis is 2 Å and the x-axis is approximately 4 Å. The red position in the sample is clearly in the range of approximately 1.8 Å, which indicates that there may be Ni−N and Ni−O bonds in Ni−COF. Furthermore, because of the wide x-axis distribution of this position, there are two shells in one peak, that is, two different coordination. This result is consistent with the fitting result. Additionally, there is no Ni−
Ni bond at the position of the x-axis greater than 5 Å, which indicates that there are only Ni−O and Ni−N bonds around the Ni atom in the sample. The above data confirm that the Ni-Salen unit exists in Ni−COF. It is worth mentioning that the materials containing the Ni−N2O2 catalytic center exhibit excellent electrocatalytic performance. For example, Zhang’s group reported excellent carbon-supported NiII single-atom catalysts and demonstrated that precise Ni−N2O2/C coordination was key to its oxygen reduction performance.17

Electrochemical Experiments for the OER

Oxygen evolution reaction (OER) activities of the M−COFs (M = Zn, Fe, Co, Ni, Cu) were investigated by steady-state linear sweep voltammetry (LSV) using a typical three-electrode system in O2-saturated 0.1 M KOH. To improve the conductivity of the electrocatalysts, a certain amount of acetylene black was mixed with COF powder. As shown in Figure 4a, the LSV of Ni−COF exhibits the best electrocatalytic activity toward the OER, having the lowest overpotential of 335 mV to achieve a 10 mA cm−2 current density (Co−COF: 347 mV; Fe−COF: 369 mV; Zn−COF: 359 mV; and Cu−COF: 384 mV; $E_0^{H_2O/O_2} = 1.229$ V is chosen as the reference). The catalytic OER kinetics of the M−COFs were investigated from the Tafel plots that were calculated from the polarization curves in Figure 4a. As shown in Figure 4b, Ni−COF exhibits a lower Tafel slope (55 mV dec−1) than Zn−COF (103 mV dec−1), Fe (78 mV dec−1), Co−COF (69 mV dec−1), and Cu−COF (72 mV dec−1), revealing the much faster reaction kinetics of Ni−COF. The electrochemical impedance spectroscopy plots were fitted in Figure 4c to calculate the charge transfer resistance ($R_{ct}$) of the OER process. The $R_{ct}$ value of Ni−COF is 72 Ω, which is smaller than that of Zn−COF (103 mV dec−1), Fe−COF (128 Ω), Co−COF (92 Ω), and Cu−COF (142 Ω). This result indicates that Ni−COF has the fastest charge transfer rate among the tested M−COFs (M = Zn, Fe, Co, Ni, Cu). These results also show that the addition of a certain amount of acetylene black can effectively improve the conductivity of the electrocatalysts, thereby improving OER performance.32,33

Figure 4. OER performances of the M−COFs (M = Zn, Fe, Co, Ni, Cu). (a) LSV curves, (b) Tafel plots, (c) EIS curves, and (d) ECSA evaluation of the M−COFs. (e) i−t curve for Ni−COF at 10 mA cm−2. (f) Free energy profiles of the OER pathway with the M−COF. (g) Catalytic cycles of oxygen evolution reaction. (h) Relationship between the overpotential and Abs($\Delta G_A - \Delta G_C$). The inset shows the optimal structures for OER catalyst under the screening criteria $\eta < 0.6$ eV, and Abs($\Delta G_A - \Delta G_C$) < 0.2 eV.
The electrochemical active surface area (ECSA) was evaluated by calculating the electrochemical double-layer capacitance \((C_{dl})\) and Figure 4d and Figure S17). As shown in Figure 4d, Ni−COF has the highest \(C_{dl}\) value of 3.79 mF cm\(^{-2}\), which is superior to that of Co−COF (2.39 mF cm\(^{-2}\)), Fe−COF (2.24 mF cm\(^{-2}\)), Cu−COF (1.02 mF cm\(^{-2}\)), and Zn−COF (0.48 mF cm\(^{-2}\)). The best electrocatalytic OER activity of Ni−COF might be related to it having the largest \(C_{dl}\) value, which leads to better effective accessibility of the active sites, resulting in outstanding OER performance. To evaluate the stability of the Ni−COF, cyclic voltammetry (CV) curves were first tested for 1000 cycles at a scan rate of 100 mV s\(^{-1}\). The LSV polarization curve after 1000 cycles is comparable to the initial curve and shows little attenuation in current density. The long-term durability of Ni−COF was also confirmed by chronoamperometry technology at a current density of 10 mA cm\(^{-2}\). The \(i−T\) curve of Ni−COF as shown in Figure 4e, demonstrates varying degrees of variation over 65 h, further revealing its good stability during electrochemical testing.

**PERSPECTIVES AND CONCLUSION**

In this work, DFT calculations show that the order of the \(ΔG\) value for the determining step of \(M\)−Salen (\(M = Zn, Fe, Co, Ni, Cu\)) follows Zn < Cu < Fe < Ni ≈ Co (Figure 4f), which is consistent with the experimental results except for the order of the catalytic OER activities of Co−COF and Ni−COF. The DFT calculations predict that the OER activities of Co and Ni are similar according to their overpotentials (the difference in \(ΔG\) for the determining step is only 7 meV, which is within the calculation error range), but the experimental results show that Ni is better than Co. This difference indicates that it is not enough to use only the Gibbs free energy change of the step to evaluate the catalytic OER activity of the catalyst. We need to introduce other features to evaluate the catalytic OER activity of the catalysts. According to Qiao’s work, \(^{32}\) the ideal catalyst should bind the reaction intermediates neither too strongly nor too weakly. Therefore, at \(U = 0\), the optimal overall reaction pathway should follow the ideal relationship of \(ΔG_A = ΔG_C\) (Figure 4g). Thus, an ideal OER catalyst should not only have a low overpotential but should possess similar \(ΔG_A\) and \(ΔG_C\) values. We define the deviation value as \(Abs(ΔG_A−ΔG_C)\). Therefore, an ideal OER catalyst should minimize the overpotential and \(Abs(ΔG_A−ΔG_C)\). Figure 4h shows the relationship between the overpotential and \(Abs(ΔG_A−ΔG_C)\). Although the Se−N\(_2\)O\(_2\)-3 system possesses a lower overpotential (0.39 eV), the \(Abs(ΔG_A−ΔG_C)\) of Se−N\(_2\)O\(_2\)-3 is as large as 0.70 eV, which corresponds to lower catalytic OER activity. We redefine the screening criteria as a lower overpotential than 0.6 eV, and the difference in Gibbs free energy \(Abs(ΔG_A−ΔG_C)\) lower than 0.2 eV. On the basis of this standard, seven top-performing materials for the OER are obtained: Fe−N\(_2\)O\(_1\)-1, Fe−N\(_2\)O\(_1\), Co−N\(_2\)O\(_2\), Ni−N\(_2\)O\(_2\), Ni−N\(_2\)O−1, Ni−N\(_2\)O\(_2\)-1, and Fe−N\(_2\)O\(_2\). Notably, although Ni−N\(_2\)O\(_2\) and Co−N\(_2\)O\(_2\) possess close overpotentials, the \(Abs(ΔG_A−ΔG_C)\) of Ni−N\(_2\)O\(_2\) is significantly lower than that of Co−N\(_2\)O\(_2\), which promotes its better OER performance. The new prediction criteria that the best material for the OER is still Fe−N\(_2\)O\(_1\)-1 with an overpotential of 0.35 eV and \(Abs(ΔG_A−ΔG_C)\) of 0.06 eV. However, under the current experimental conditions, we have not been able to synthesize Fe−N\(_2\)O\(_1\)-1. With the development of experimental science, we believe it will be synthesized in the future.

To conclude, we systematically examined the OER activity of a series of simplified model catalysts by means of comprehensive DFT calculations and a ML method. The results showed that several experimentally unexplored Fe−N\(_2\)O and Co−N\(_2\)O\(_2\) model catalysts showed better OER catalytic performance. The ML study showed that the OER activity of the simplified model catalysts (N\(_2\)O−C) could be well described by the combination of four intrinsic factors. More importantly, we incorporated the M−N\(_2\)O\(_2\) (M = Zn, Fe, Co, Ni, Cu) moiety into covalent organic frameworks to prepare electrocatalysts and conducted electrocatalytic OER measurements. The experimental results highly agreed with the DFT predictions. The Ni−COF catalyst for the OER had high activity and stability with a current density of 10 mA cm\(^{-2}\) at a low overpotential of 335 mV and a small Tafel slope of 55 mV dec\(^{-1}\). The experimental studies show that Ni−COF is among the best of COF-based OER catalysts reported to date (Figure S19). The findings not only suggest an effective method for the synthesis of metal-containing COF-based electrocatalysts but also provide a deep understanding of material design by combining the theoretical and experimental results regarding the OER.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00258.

Chemical and physical characterizations of Salen−COFs; synthesis process of Salen−COFs; electrochemical characterizations; density functional theory calculation details; free energy diagram for OER on M−N\(_2\)O\(_2\); calculated Gibbs free energy changes and adsorption free energy changes for intermediates of OER; 23 initial features with description; figures and tables for chemical and physical characterizations and OER catalytic activity test (PDF)

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Author Contributions
W.Z. and L.Y. contributed equally to this work. L.S. and W.Q.D. planned and designed the project. L.Y. and D.Z. executed the theoretical screening. W.Z. and L.Y. built COFs. W.Z., W.L.Z., J.X.Y., and W.X. conducted the catalytic experiments. W.Q.D. planned and designed the project. L.Y. and D.Z. performed the theoretical calculations. W.Z., W.L.Z., J.X.Y., and W.X. conducted the catalyst activity evaluation, adsorption characterization, and spectroscopy. All authors were involved in the writing of the manuscript.

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Notes
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