

Electrochemical Instability of Metal-organic Frameworks: *In Situ* Spectroelectrochemical Investigation of the Real Active Sites

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ABSTRACT: Despite recent attempts using metal-organic frameworks (MOFs) directly as electrocatalysts, the electrochemical stability of MOFs and the role of *in situ* formed species during electrochemistry are elusive. Using *in situ* spectroelectrochemistry, we present herein a comprehensive discussion on the structural and morphologic evolution of MOFs (zeolitic imidazolate framework-67, ZIF-67) during both cyclic voltammetry and amperometry. Dramatic morphologic changes exposing electron-accessible Co sites are evident. The intense conversion from tetrahedral Co sites in ZIF-67 to tetrahedral α -Co(OH)₂ and octahedral β -Co(OH)₂, and the formation of their corresponding oxidized forms (CoOOH), is observed during both electrochemical treatments. Subsequent oxygen evolution reaction (OER) suggests the CoOOH produced from α/β -Co(OH)₂ as the dominating active sites, not the metal nodes of ZIF-67. Specifically, the CoOOH from α -Co(OH)₂ is most active (turnover frequency = 0.59 s⁻¹), compared to 0.06 s⁻¹ from β -Co(OH)₂. Our study demonstrates the importance of examining the electrochemical stability of MOFs for electrocatalyst design.

KEYWORDS: ZIF-67, *in situ* UV-Vis, *in situ* Raman, spectroelectrochemistry, electrochemical stability, cobalt hydroxide, oxygen evolution reaction

1. INTRODUCTION

Metal-organic frameworks (MOFs), composed of metal ions or clusters coordinated with organic linker molecules, have received a spotlight in material research since the last decade due to their structural flexibility.¹ Currently, a number of tailor-designed MOFs have demonstrated high efficiencies in both energy and environmental applications, such as gas storage, separation, sensing, energy storage, and conversion.²⁻³ Especially, for the holy grail of energy-related electrocatalysis, such as CO₂ reduction and water splitting, the unique characteristics of MOFs have made them good candidates:⁴⁻⁵ On the one hand, the permanent porosity of MOFs can facilitate the rapid mass transfer of substrate and product throughout the bulk material, unleashing the limitation that restricts the reaction rate of many conventional electrocatalysts.⁶ On the other hand, the well-defined single metal sites are analogous to the molecular catalysts, enabling MOFs to act as single-atom electrocatalysts with 100% atom utilization.⁷ Moreover, the electronic properties of metal sites can be tuned by altering the linker, adding further flexibility of catalyst design towards desired performance. Based on such guidelines, various MOF-based electrocatalysts have been designed to achieve superior performances in electrocatalysis.⁸ Especially, due to the importance of the oxygen evolution reaction (OER) in water splitting, Co-MOFs,⁹⁻¹⁰ NiCo-MOFs,¹¹⁻¹³ FeCo-MOFs,¹⁴⁻¹⁵ and NiFe-MOFs¹⁶⁻¹⁷ have been extensively explored, and all of them imply the atomic metal nodes as the real active sites for oxygen production.

However, attributing electrocatalytic activity exclusively to metal nodes is valid only if the MOFs structure remains intact throughout the electrochemical processes. As recently suggested by many researchers, the *in situ* conversion of the pristine electrocatalyst during OER is critical for their high per-

formance, and the intermediates are identified as the real active sites.¹⁸ Taking Co-based electrocatalysts as an example, recent *operando* evidence suggests the conversion of Co²⁺ (Co(OH)₂ and CoO_x) to Co³⁺ (CoOOH) as a pre-catalytic electrochemical process, and both oxidized forms of Co²⁺, including Co³⁺ and Co⁴⁺, are assigned for OER activity.¹⁹⁻²⁰ In such cases, the pristine electrocatalysts are the pre-catalyst for active site production. A similar phenomenon is also likely for MOFs since the mechanism of OER requires the formation of M-OH⁻ and electrooxidation to M-OOH (M = metal),¹⁹ meaning the replacement of coordinating linker molecules by hydroxide ions. Considering that the metal-linker coordination is the backbone of MOFs, such replacements can result in partial or major structural destruction. However, despite multiple reports suggesting the formation of metal oxide in the MOFs after (during) electrocatalysis,^{17,21} the information on the electrochemical evolution of MOFs and the role of the formed structures are not available yet. Also, the co-existing *in situ* generated metal species during electrochemical treatments (*e.g.*, cyclic voltammetry (CV) and amperometry) further complicates the understanding of the real active sites.

Consequently, the interpretation of the OER activity based on *ex situ* characterizations before the electrocatalysis could be, sometimes, misleading. For example, both NiO and Fe₂O₃ polycrystalline structures are formed after the OER process using NiFe-MOFs,¹⁷ and the assignment of real active site can be difficult because both NiO and Ni/Fe nodes can provide the sites for M-OOH formation. Furthermore, such co-existence of active species can obscure the interpretation of CV and amperometry, due to the mixed redox signals arising from metal nodes and intermediates, especially when many researchers prefer to present only the ‘stable’ cycle of plots.

One strategy to address such dispute is the *in situ* techniques coupled with electrochemistry, as demonstrated previously on

other electrocatalysts. For example, Koel *et al.* used *in situ* Raman spectroscopy to identify the formation of NiOOH as the reason for improved OER activity in NiCoO_xH_y material.¹⁸ Using *operando* ambient-pressure X-ray photoelectron spectroscopy (XPS), Favaro *et al.* revealed the complete conversion of Co(OH)₂ to CoOOH before OER potential and the production of Co⁴⁺ during OER.²⁰ However, neither the *in situ* electrochemical studies of MOFs during electrochemical treatments nor the role of *in situ* formed species during the pre-catalytic electrochemical processes, as the fundamental aspect of MOF-based electrocatalysts, is available yet.

Herein, we present the first comprehensive discussion on the morphologic and structural evolution of MOFs during two typical electrochemical treatments: CV and amperometry. Zeolitic imidazole framework-67 (ZIF-67), one of the most widely used MOFs and relatively stable in an aqueous solvent, is studied as a representative demonstration. Evidence from both *in situ* UV-Vis spectra and *in situ* Raman spectra, as well as *ex situ* characterizations such as electron microscope, powder diffraction, and XPS, are discussed to unveil the full image of the evolution of ZIF-67. Finally, the role of the *in situ* formed species during pre-catalytic and catalytic processes is revealed as the dominating active sites of ZIF-67 responsible for its enhanced OER activity.

2. RESULTS AND DISCUSSION

2.1 Morphology of ZIF-67. Figure 1A shows a representative structural unit of pristine ZIF-67 hosting a pore of *ca.* 1.70 nm constructed by tetrahedral Co sites coordinated with four 2-methylimidazole (mIM) molecules (denoted as Co(mIM)₄). As the platform material, cubic ZIF-67 is obtained following an established method²² with a mean edge length of 158 nm (Figure 1B). The ZIF-67-modified carbon fiber paper (ZIF-67@CFP) electrode shows evenly coated ZIF-67 nanocubes on the carbon fiber surface (Figure 1C). MOFs are known as electron beam-sensitive crystalline materials, and their high-resolution imaging is still challenging to date.²³ The transmission electron microscopic (TEM) image (Figure 1D) and the high-resolution images of selected regions (Figures 1E, 1F, and 1G showing center, corner, and edge regions) imply no clear crystalline structure of ZIF-67, also indicated by the featureless selected area electron diffraction (SAED) patterns, such results rule out the other Co-based structures. It is worth to note that no significant electron beam damage is observed during the imaging of pristine ZIF-67 at 200 kV even with a relatively long imaging time (6 min), nor any other crystalline structures. (Supplemental movie 1). Elemental mappings on a dark-field TEM image (Figure 1H) suggest uniformly distributed Co, N, and O, and the presence of O is attributed to the physisorbed H₂O and OH.

2.2 CV pre-catalytic treatment. The CV is one of the most popular and fundamental techniques to study the electrochemical properties of materials. During a typical CV study, a cycling external potential is applied on the surface of the modified electrode, promoting the formation of electrochemical double layer and/or electron exchanges between electrode and electrolyte. Various reactions, including chemical and redox processes, occur during CV treatment depending on the applied potential. Needless to say, the reliability of CV profiles is based on the presupposition that modified electrodes are stable during CV treatment.

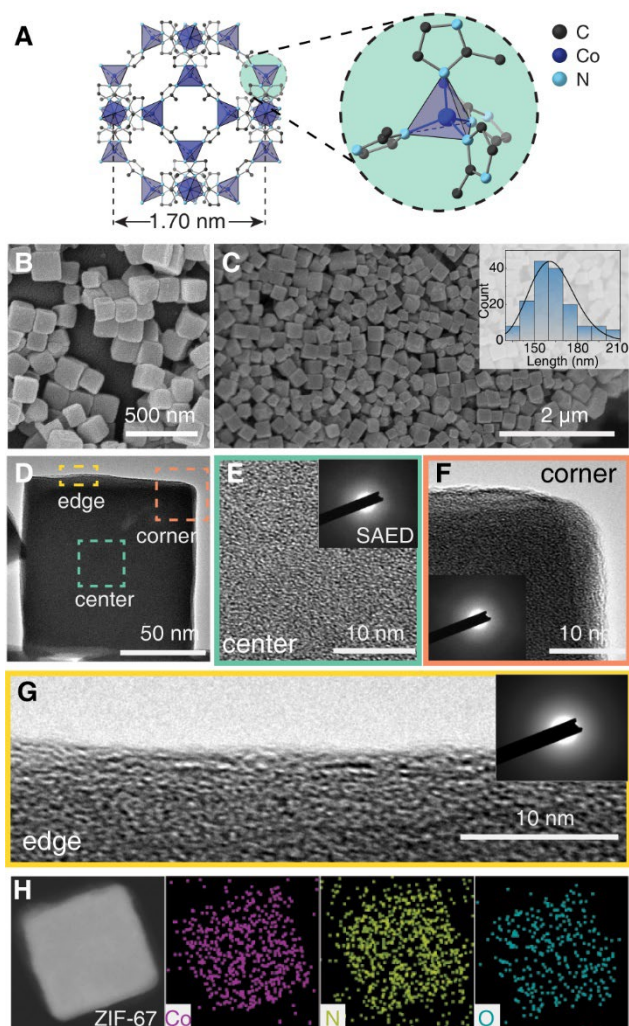


Figure 1. Morphology of ZIF-67@CFP electrode. (A) A representative structural unit of pristine ZIF-67 showing the tetrahedral Co site. (B-C) SEM images of (B) ZIF-67 nanocube and (C) surface of the ZIF-67@CFP electrode. The inset shows the size distribution. (D-G) TEM images of (D) a single ZIF-67 nanocube and its (E) center, (F) corner, and (G) edge regions. Inset shows the SAED patterns of the selected region. (H) Dark-field TEM image of a nanocube and its corresponding Co, N, and O elemental mapping.

Therefore, to verify the presupposition, we performed CV treatment in 1.0 M KOH electrolyte for 100 cycles using the ZIF-67@CFP electrode. Moreover, the CV of ZIF-67 is studied within three potential windows (0.925-1.025 V (denoted as **0.1**), 0.925-1.325 V (denoted as **0.4**), and 0.925-1.525 V (denoted as **0.6**), vs. RHE), to separate different electrochemical processes accompanying the potential change.

Within **0.1**, the ZIF-67@CFP electrode shows a typical capacitor behavior (Figure 2A) where the non-Faradic charge/discharge currents increase from the first to 60th cycles and stabilize thereafter. Considering that the current mainly arises from the adsorption and release of hydroxide ions within the double-layer region for capacitors, the increasing trend

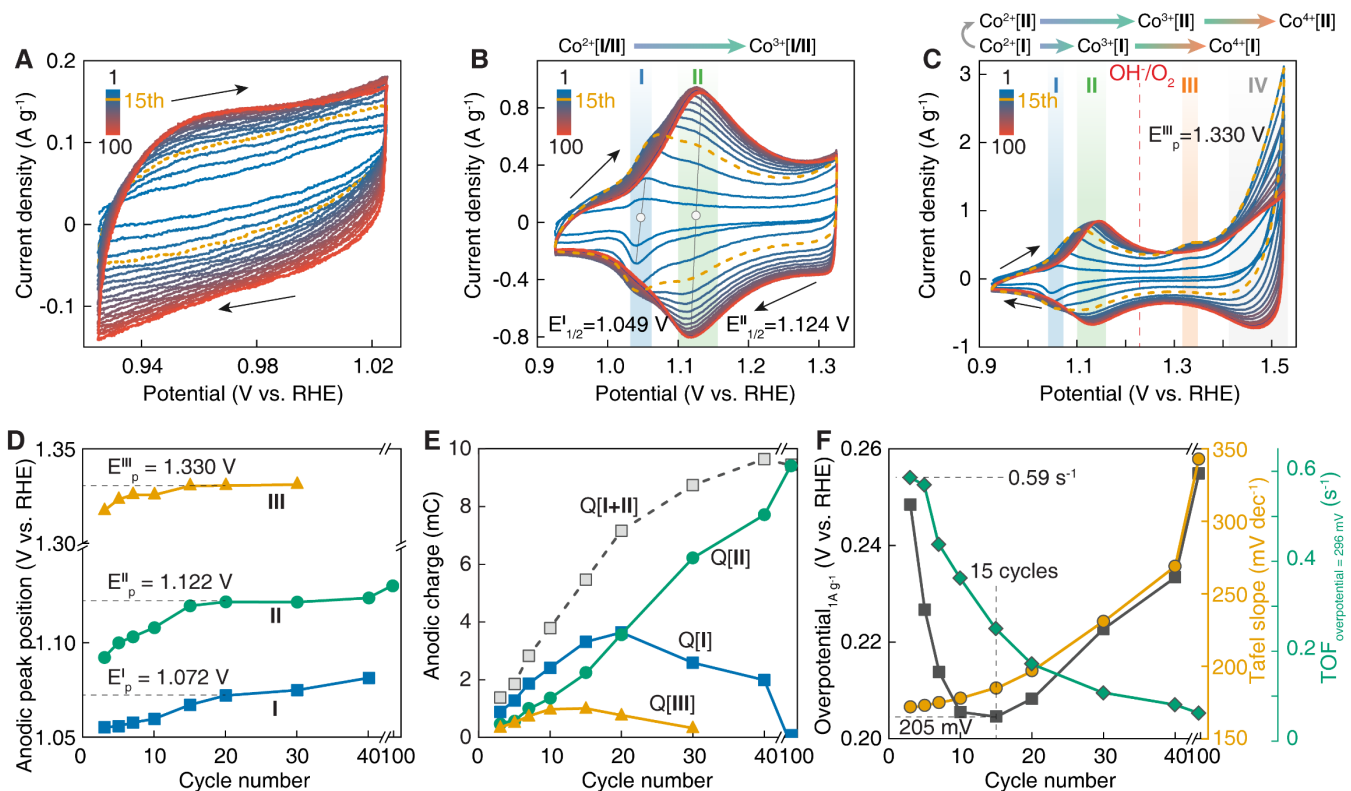


Figure 2. CV study of ZIF-67@CFP electrode. Continuous cyclic voltammograms (1, 5, 10..., 100) of ZIF-67@CFP electrode in 1.0 M KOH electrolyte between (A) 0.925-1.025 V, (B) 0.925-1.325 V, (C) 0.925-1.525 V. Scan rate is 10 mV s⁻¹. The 15th scan is highlighted as yellow dotted lines. Plots showing the change of (D) anodic peak position, (E) anodic charge, and (F) OER overpotential (current density = 1 A g⁻¹), Tafel slope, and TOF (overpotential = 296 mV) with cycle number.

of the current suggests the growth of the electrochemical surface area (ECSA) of ZIF-67 with cycle numbers. Moreover, the kinetic aspects of the OH⁻ ion diffusion can be revealed by electrochemical impedance spectroscopy (EIS). For a stable porous material, the phase angle of the straight line in the mid-frequency region is mainly controlled by the material morphology and the surface area,²⁴ and large phase angle value indicates fast ion diffusion. **Figure S1A** shows the Nyquist plots of the ZIF-67@CFP electrode cycled within **0.1**. Before cycling, the phase angle is larger than 45° in the mid-frequency region deviating from the Warburg diffusion element, representing a high OH⁻ diffusion rate possibly due to the porous trait of MOFs and rapid coordination between OH⁻ and Co sites in the pores. During CV cycling, the phase angle decreases first (0-30 cycle) and increases back slightly (30-100 cycle). Such a trend indicates the same change in OH⁻ diffusion behavior. The initial drop can be related to the morphologic evolution of ZIF-67 (possible loss of pore of *ca.* 1.70 nm), while the following increment to the establishment of new microstructures with better OH⁻ adsorption/desorption capability. However, since the molecule structure of ZIF-67 could be unstable during the CV study, the detailed reason behind the kinetic trend of ion diffusion can be more complicated.

At a wider potential window of **0.4** (**Figure 2B**), apart from the increasing ECSA, two recognizable redox couples (marked as region **I** and **II**) with half-wave potentials (E_{1/2}) at 1.049 and 1.124 V evolve until the 40th cycle. Both can be attributed to the redox between Co²⁺ and Co³⁺ species, yet the different E_{1/2} values indicate the existence of two Co²⁺ species (We denote them as Co²⁺[**I**] and Co²⁺[**II**] temporarily here to avoid

confusion, until they are confirmed as α- and β-Co(OH)₂, respectively, in section 2.4). Moreover, the increasing anodic peak current suggests the continuous exposure of more accessible Co sites. After 40 cycles, only the redox couple at 1.124 V remains with the plateaued anodic peak current, indicating the MOF structure is converted to a CV-stable structure. Notably, incomplete reduction of Co³⁺ species is suggested by the larger anodic peak current than cathodic one (for example, at the 40th cycle, anodic: 0.537 A g⁻¹; cathodic: 0.411 A g⁻¹). The phase angle first decreases until the 15th cycle and slightly increases from the 16th to 100th cycles (**Figure S1B**). The initial decline marks the porosity loss of MOFs, while the subsequent rise could be reasoned by the production of Co-based microstructure after CV pre-catalytic treatment. A new anodic peak (peak potential E_p = 1.330 V, marked as region **III**) appears after cycling within **0.6** (**Figure 2C**), indicating the electrooxidation of Co³⁺ to Co⁴⁺ species. Unlike **I** and **II**, region **III** shows no corresponding cathodic peak, mainly because the unstable Co⁴⁺ species can rapidly undergo a coupled chemical reduction to Co³⁺.¹⁹ Apart from the pre-catalytic **I**, **II**, and **III** regions, the catalytic OER occurs at a higher potential (region **IV**) and reaches the maximum current between the 15th and 20th cycles. Similar to the CV treatment within **0.4** but in a swifter fashion (phase angle drops and rises in fewer cycle numbers), the phase angle (**Figure S1C**) declines until the 5th cycle and rises between the 6th and 10th cycles, while further cycles bring negligible changes. The 100th cycle shows a higher phase angle of 76° compared to 65°. Therefore, the CV pre-catalytic treatment at a wider potential range *i.e.*, **0.6**, not only causes the quick destruction of MOF porosity but also the fast production of new porous Co-based structure.

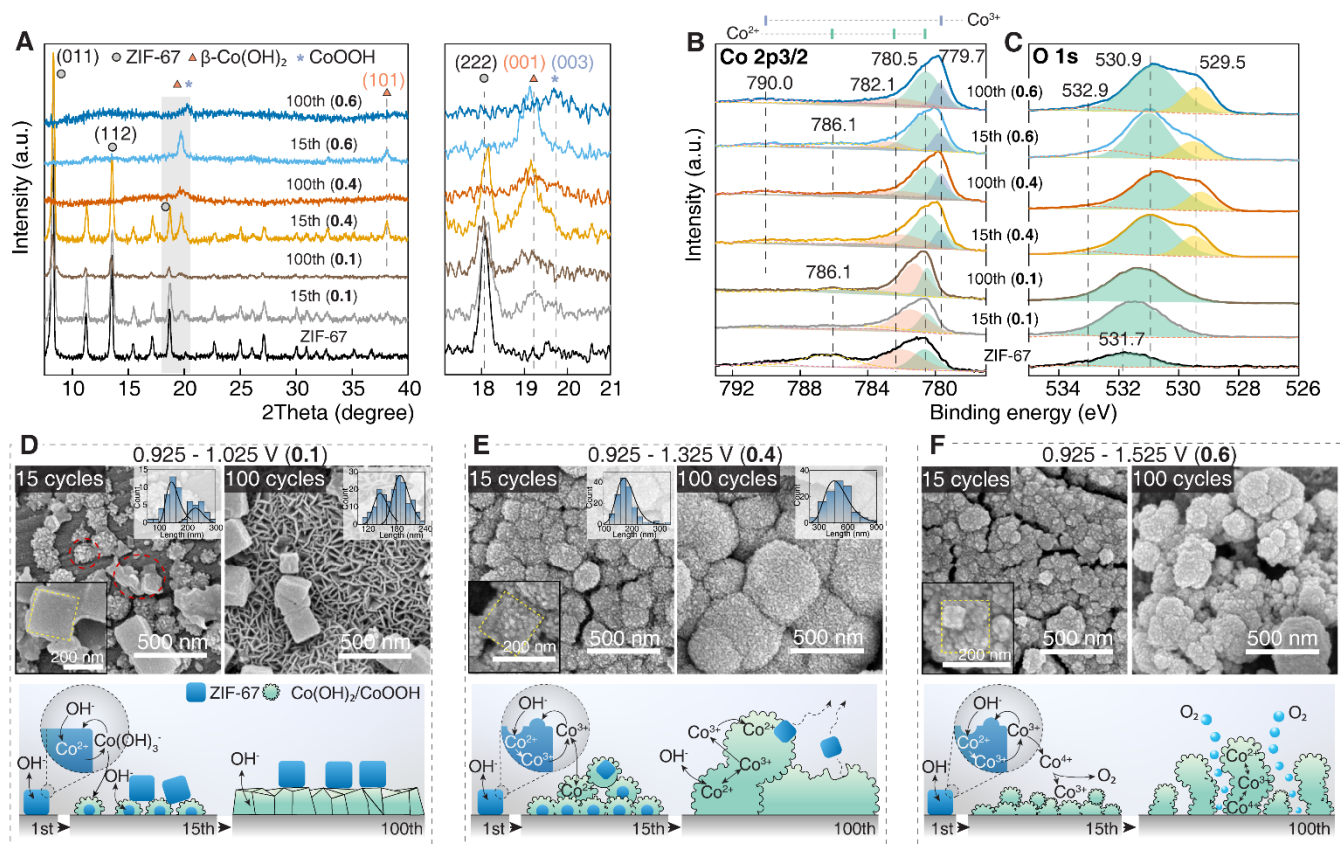


Figure 3. Structure and morphology of ZIF-67@CFP electrode after CV treatment. (A) XRD pattern of pristine and CV-treated ZIF-67 with different cycles (15 and 100) between different potential ranges: **0.1** (0.925-1.025 V), **0.4** (0.925-1.325 V), and **0.6** (0.925-1.525 V). The zoom-in view emphasizes ZIF-67 (222), β -Co(OH)₂ (001), and CoOOH (003). (B-C) XPS spectra of (B) Co 2p_{3/2} and (C) O 1s region of pristine and CV-treated ZIF-67 with different cycles (15 and 100) between different potential range: **0.1**, **0.4**, and **0.6**. SEM images of ZIF-67 after CV treatment and the corresponding illustration of structural evolution between (D) **0.1**, (E) **0.4**, and (F) **0.6** for 15 and 100 cycles. The insets show the zoom-in view and size distribution.

By deconvoluting the CV plots (example shown in Figure S2), both peak position and charge of the three anodic peaks in the regions I, II, and III can be quantitated. As potential cycling proceeds (Figure 2D), all peaks shift to higher potential values until the 20th cycle and stabilize at 1.072, 1.122, and 1.330 V, respectively. Such peak shifting could be understood by the collective effect of larger ECSA (thus increased number of Co²⁺ species) and the structural evolution of Co²⁺ to its stable form (thus higher oxidation potential). The anodic charges shown as Q[I] and Q[II] for anodic peak I and II in Figure 2E denote the numbers of electron-accessible Co²⁺ sites. The up-rising trend of Q[I] observed in the first 20 cycles implies the increasing concentration of Co²⁺[I] species, while further cycles decrease its total number. Q[II], however, continues to increase with cycle numbers throughout the entire CV studies. The increment between the first and 20th cycles indicates that both Co²⁺ species are exposed as a result of CV treatment, yet the declining trend of Q[I] shows that Co²⁺[I] is unstable during CV and can be converted, possibly, to Co²⁺[II]. Q[I+II], representing the total amount of electrochemically accessible Co²⁺ species, shows an increasing trend between the first and 40th cycles, rendering the continuous exposure of Co²⁺ species. After 40 cycles, the total anodic charge reaches 9.80 mC (1.02×10^{-4} mmol of Co²⁺), which is merely 1.3% of the total Co²⁺ (7.92×10^{-3} mmol) on the electrode. Since the oxidation of Co²⁺ to Co³⁺ requires both electrons and OH⁻, such a low percentage shows that only the surface Co²⁺ species can be

accessed by electrons and OH⁻ during the CV treatment. Further cycling to 100 cycles results in the negligible changes to 9.45 mC, an indication of established ECSA and stable surface Co²⁺ species. The Co³⁺ to Co⁴⁺ electrooxidation charge, denoted as Q[III], follows a similar trend as Q[I], reaching the maximum at the 15th cycle and completely disappearing after 30 cycles. Such correlation between Q[I] and Q[III] indicates that they are related to the continuous electrooxidation of the same Co²⁺ species: $\text{Co}^{2+}[\text{I}] \xrightarrow{\text{Q}[\text{I}]} \text{Co}^{3+}[\text{I}] \xrightarrow{\text{Q}[\text{III}]} \text{Co}^{4+}[\text{I}]$. The Co³⁺[II] to Co⁴⁺[II] electrooxidation signal is overlapping with OER catalytic current, thus it is not differentiable. Therefore, instead of acting as an electrocatalyst, ZIF-67 is more like a pre-catalyst, and the pre-catalytic CV process can produce two electron-accessible Co²⁺ species with different Co²⁺-Co³⁺-Co⁴⁺ oxidation potentials.

The impact of pre-catalytically produced species on the catalytic OER process is presented in Figure 2F, where the change in OER properties is given in correlation with the CV cycle number. Since the pre-catalytic conversion of Co²⁺ to Co³⁺ and Co⁴⁺ is electrochemically inevitable and both Co³⁺ and Co⁴⁺ are considered as the real active sites,²⁰ we use Co[I] and Co[II] in the following context to represent the oxidized forms of Co²⁺[I] and Co²⁺[II] for clarification. The declining trend of TOF at an overpotential of 296 mV shows that the normalized activity of Co sites decreases from 0.59 s⁻¹ (after 3 cycles) to 0.06 s⁻¹ (after 100 cycles) with a 90% activity loss.

The continuous transformation from more active Co[I] to less active Co[II] species is thus suggested, leading to the collective activity drop of Co sites. Notably, the TOF value at the 3rd cycle is 6 times higher than the previously reported Co chalcogenide.²⁵ Also, the Tafel slope (Tafel plot shown in **Figure S3**) increases with the cycle number, showing a decreasing OER kinetic rate after more CV stripping. The lowest overpotential for a current density of 1 A g⁻¹ is 205 mV after 15 cycles. The inverted volcano-type trend of overpotential is jointly decided by the total number of active sites and the activity of a particular site: at lower cycle numbers, only limited concentration of Co²⁺ species as the pre-catalyst is available for OER; at higher cycle numbers, active Co[I] sites are completely converted to relatively inactive Co[II] sites.

2.3 Structural and morphologic evolution of ZIF-67 during CV pre-catalytic treatment. As shown in **Figure 3A**, the *ex situ* X-ray powder diffraction (XRD) pattern of pristine ZIF-67 matches well with the previous report,²⁶ where two intensive peaks at 7.4° and 12.8° are assigned to (011) and (112) facets, respectively. The pattern of ZIF-67 is retained after both 15 and 100 cycles between 0.925 and 1.025 V (**0.1**). The broadening of (011) peak, however, indicates that crystallite size is decreased. A minor peak appears at 19.2° after 15 cycles, representing the (001) plane of β -Co(OH)₂ (JCPDS 30-0443).²⁷ At a wider window of **0.4**, besides the β -Co(OH)₂ verified by its (001) and (101) facets at 19.2° and 38.1°, respectively, the electrooxidation of Co²⁺ to Co³⁺ starts, as confirmed by the distinct formation of CoOOH (shoulder peak at 19.7° attributed to its (003) plane (JCPDS 78-11213)).²⁷ The ZIF-67 peaks have vanished after 100 cycles. Further expansion of potential window to **0.6** leads to the complete devastation of ZIF-67 after only 15 cycles. The dominating β -Co(OH)₂ after 15 cycles have changed to CoOOH after 100 cycles as indicated by the single peak at 19.7°. Therefore, the ZIF-67 structure is unstable during CV treatments, eventually converted to β -Co(OH)₂ and CoOOH, depending on the CV potential windows.

The presence of Co, N, and O species on the surface of the electrode before and after CV pre-catalytic treatment was confirmed by the XPS (**Figure S4A**). The pristine ZIF-67 shows a surface N-to-Co atomic ratio of 3.63, slightly lower than the stoichiometric number of 4. It is likely that a portion of surficial Co coordination sites is occupied by the physisorbed H₂O. Shown in **Table S1**, the CV pre-catalytic treatments lead to the dramatic decrement of N-to-Co ratio to 0.77 (15 cycles within **0.1**), 0.62 (15 cycles within **0.4**), 0.69 (15 cycles within **0.6**), and eventual to 0.39 (**0.1**) and 0.21 (**0.4** and **0.6**) after 100 cycles, revealing the destruction of ZIF-67. Meanwhile, the rapid drop of surface N-to-O ratio from 4.81 to 0.13 (**0.1**) and 0.08 (**0.4** and **0.6**) after 100 cycles confirms the replacement of surface coordinating N-containing linker molecules (loss to electrolyte during CV) by OH⁻/O²⁻ after the pre-catalytic electrochemical process. Such replacement is also suggested by the reduced N 1s peak after CV treatment (**Figure S4B**).

Examining the Co 2p_{3/2} peak of pristine ZIF-67 (**Figure 3B**) reveals three peaks at 780.5, 782.1, and 786.1 eV. The former two peaks are ascribed to the surface Co species coordinated with OH⁻ and mIM linkers, and the last to the satellite peak. The distance between the satellite peak and the main peaks are 5.6 and 4.0 eV, indicating that all Co species of ZIF-67 is in the form of Co²⁺.²⁸⁻²⁹ Within **0.1**, no significant evolution of

the Co²⁺ signal is observed after 15 and 100 cycles, showing no valence changes. After the CV treatment involving the redox between Co²⁺-Co³⁺ (**0.4**) and Co²⁺-Co³⁺-Co⁴⁺ (**0.6**), a new peak at 779.7 eV, assigned to the Co³⁺ species, evolves from all samples, as well as another satellite peak at 790.0 eV. The distance between the two new peaks is 10.3 eV, confirming the existence of Co³⁺ species,³⁰ in good agreement with the XRD results of finding CoOOH (**Figure 3A**). Meanwhile, both physisorbed H₂O (532.9 eV) and OH⁻ (531.7 eV) exist on the surface of pristine ZIF-67 (**Figure 3C**). A single peak of OH⁻ is observed after cycling within **0.1**, which shifts slightly from 531.5 eV (15 cycles) to 531.1 eV (100 cycles). Such peak shifting can be reasoned by the gradual structural transition from Co-OH within the ZIF-67 coordination environment to crystalline Co(OH)₂.

After cycling within higher potential windows (**0.4** and **0.6**), the oxide ions (O²⁻) from CoOOH is evident by the peak at 529.5 eV,³⁰ accompanied by the shifting of OH⁻ peak to 530.9 eV. Such shifting indicates the different coordination environments of OH⁻ species on tetrahedral ZIF-67 (the initial structure) and octahedral β -Co(OH)₂ (the final structure). Notably, despite finding OH⁻ in ZIF-67 structure by XPS, no Co(OH)₂ structure is suggested by the XRD result, indicating that only neglectable mIM linkers are replaced by OH⁻ while the Co coordination configuration of ZIF-67 remains as the pristine state. Since the first cycle of ZIF-67 shows mainly Co²⁺[I] oxidation signal (**Figure 2B**), we believe that OH⁻ signal observed from XPS originates from the minor Co²⁺[I].

Dramatic morphologic changes induced by CV are shown by the scanning electron microscopic (SEM) images in **Figures 3D-F** (Zoom-out images of a single CFP shown in **Figure S5**). With only the capacitive process involved within **0.1**, the deformation of ZIF-67 nanocubes is observed after 15 cycles, forming smaller island-like nanoparticles (*ca.* 145 nm mean diameter) which further transforms into vertically aligned nanosheets at the 100th cycle. The nanosheets are β -Co(OH)₂ structure as indicated by previous XRD results, and a similar morphology was also reported from the electrodeposited β -Co(OH)₂.³¹ The transition process is illustrated in **Figure 3D** where hydroxide ions travel into the porous ZIF-67 structure during the anodic scan (charge process) and replace the mIM linker to form Co(OH)₃⁻ ions. The reverse cathodic scan forces Co(OH)₃⁻ out of the framework (discharge process), destroying the ZIF-67 structure. Another anodic scan attracts Co(OH)₃⁻ on the surface of carbon fiber to form Co(OH)₂ structure, similar to the electrodeposition process. The formation of such a nanosheet structure with high ECSA also explains the increased capacitance in **Figure 2A**. Surprisingly, some of the nanocubes persist after 100 cycles, presumably because only the ZIF-67 nanocubes in direct contact with CFP can be accessed by electron and potential, thus are subject to the potential-driven OH⁻ sorption and Co(OH)₃⁻ desorption. When the Co²⁺-Co³⁺ redox processes are involved (within **0.4**), the final β -Co(OH)₂ structure tends to adopt a spherical shape with a mean diameter of 164 nm at the 15th cycle which grows to 477 nm after 100 cycles. The deformed nanocubes act as nucleation sites on which the produced CoOOH can be reduced. The cubic vacancies observed in **Figure S6** supports such an explanation. As the potential window reaches **0.6**, the oxidation of Co³⁺ to Co⁴⁺ actuates, followed by O₂ discharge. The cracks formed after 15 cycles and pores after 100 cycles are due to the evolution of O₂ from Co sites. Such morphology makes it practically impossible to analyze the particle size.

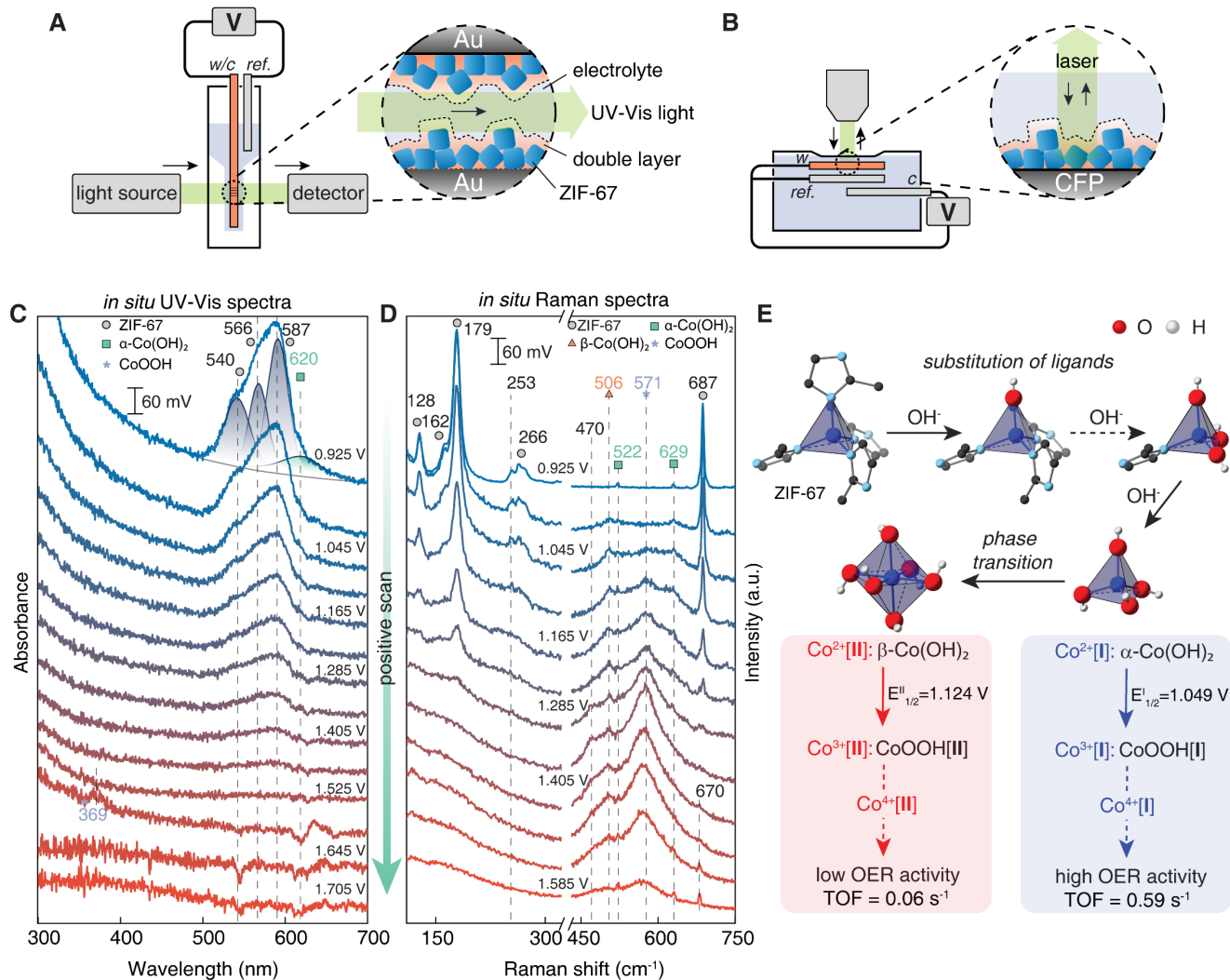


Figure 4. *In situ* spectroelectrochemical studies of ZIF-67 and proposed structural evolution. (A-B) Simplified cell configuration and sampling of the electrode surface during (A) *in situ* UV-Vis experiment, (B) *in situ* Raman experiment. *w* = working electrode, *c* = counter electrode, and *ref.* = reference electrode. (C) *In situ* UV-Vis spectroelectrochemical study between 0.925-1.705 V. (D) *In situ* Raman spectroelectrochemical study between 0.925-1.585 V. Only forward scans are shown. The sampling interval is 60 mV. (E) Illustration of the pre-catalytic conversion of ZIF-67 to α -Co(OH)₂ and β -Co(OH)₂, and their further oxidation and OER activity.

Therefore, as proved by the *ex situ* characterization after CV studies, the ZIF-67 is converted to β -Co(OH)₂ and CoOOH structure as the final form, depending on the potential windows. However, the intermediated species between such conversion needs to be revealed by *in situ* studies.

2.4 *In situ* spectroelectrochemistry of the first CV cycle. To understand the pre-catalytic transition of Co sites with tetrahedral coordination in ZIF-67 to octahedral in β -Co(OH)₂ and the assignment of Co²⁺[I] and Co²⁺[II], *in situ* spectroelectrochemical methods, including *in situ* UV-Vis and Raman spectroscopy, are employed to investigate the first cycle. The *in situ* electrochemical cells of both techniques and the integrated polarization curves are shown in **Figures S7A** and **S7B**. To clarify, the simplified cell configurations and sampling processes during the *in situ* spectroelectrochemistry are shown in **Figures 4A** and **4B**. For *in situ* UV-Vis spectroscopy, a transmission configuration was used, in which UV-Vis light travels through the Au-coated tunnels of the working electrode (Au honeycomb electrode) to reach the detector. During the experiment, the tunnels are coated with a layer of ZIF-67 particles.

As a result, the UV-Vis light can collect structural information by interacting with the species on the surface of the electrode and in the double layer. The *in situ* Raman experiment, on the other hand, adopts a similar configuration to the one for *ex situ* Raman tests except for an *in situ* cell to perform electrochemistry. The structural information of the bulk ZIF-67 and its surface species are collected during the electrochemical experiments.

Figure 4C shows the UV-Vis spectra of ZIF-67 at various applied potentials. At 0.925 V, in addition to the uprising absorption <400 nm caused by the mIM linker, the broad absorption signal is obvious from 500 to 650 nm which can be resolved to four peaks using Gaussian functions.³² The three main peaks at 540, 566, and 587 nm are known as the spin-orbital coupling triplet peaks, which can be assigned to the ⁴A₂(F) to ⁴T₁(P) transition of tetrahedral Co sites.³³ The absence of any peaks at 480 and 506 nm rules out the existence of any octahedral Co coordination in ZIF-67.³⁴ The minor peak at 620 nm matches the adsorption edge of α -Co(OH)₂ which also features a tetrahedral Co coordination.³⁵ The formation of

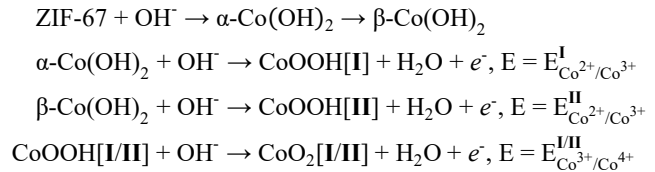
α -Co(OH)₂ could be attributed to the coordination of surface Co with H₂O during synthesis. In the positive scan from 0.925 to 1.705 V, the intensity of the triplet peaks gradually decreases until vanishes at 1.525 V, and the peak at 620 nm persists until 1.465 V. The decrement indicates the destruction of surface tetrahedral coordination environment in ZIF-67, and the decreased absorption <400 nm also confirms the loss of mIM linkers. As demonstrated by previous electrochemical and *ex situ* characterization results, the MOF structure sequentially undergoes Co²⁺ → Co³⁺ → Co⁴⁺ electrooxidation and oxygen evolution with increasing potential. Therefore, the destruction could be attributed to the potential-driven formation of CoOH⁻ coordination and/or Co²⁺ to Co³⁺ electrooxidation. Notably, as the potential rises from 1.525 to 1.585 V, a zig-zag signal evolves at around 630 nm, which can be resolved to at least two overlapping peaks (one decreasing while the other increasing). On one hand, the decreasing signal agrees with the peak of α -Co(OH)₂ at 620 nm, therefore representing the rapid consumption of α -Co(OH)₂. On the other hand, the increasing peak can be related to the CoOOH produced *via* electrooxidation. The generation of Co³⁺ species is also confirmed by an intense signal at 369 nm appears at 1.585 V.³⁴ It is thus convincing that the produced Co³⁺ species is originated from α -Co(OH)₂, meaning that the previously identified Co²⁺[I] species is most likely α -Co(OH)₂. However, it should be noted that the Co³⁺ production occurs at a much lower potential (*ca.* 1.04 V, **Figure 2B**). The absence of Co³⁺ signal below 1.585 V (but above the E_{Co²⁺/Co³⁺}) is most likely due to the relatively low concentration of Co³⁺, which accumulates and becomes detectable from 1.585 V.

At higher potentials (1.645 and 1.705 V), the Co³⁺ signal disappears due to the subsequent Co³⁺ electrooxidation to Co⁴⁺. Furthermore, a reverse scan (**Figure S7C**) does not make the Co³⁺ disappear nor revive the trait peaks of ZIF-67, indicating the irreversible structural destruction of ZIF-67. No significant β -Co(OH)₂ signal is found, possibly due to its minor signal compared to the noise contributed by the produced O₂ bubbles at high potential.

The *in situ* Raman spectroelectrochemistry provides more sensitive real-time insights into the structural evolution process. A low laser power (1.5 mW) is applied to avoid phase transitions from CoOOH to Co₃O₄ triggered by laser heating.³⁶ The region between 100 and 750 cm⁻¹ reflecting the lattice vibrations is shown in **Figure 4D**. The characteristic Raman peaks of ZIF-67 at 162 and 179 cm⁻¹ are attributed to the nitrogen-cobalt-nitrogen (N-Co-N) deformation vibration modes,³⁷ and the peaks at 266 and 687 cm⁻¹ to the C-CH₃ stretching of mIM linker molecules.³⁸ At 0.925 V, the minor peak at 629 cm⁻¹ is assigned to the E_g vibration mode of α -Co(OH)₂, while the absence of A_{2u} mode (*ca.* 501 cm⁻¹) implies no β -Co(OH)₂.³⁹ The peak at 522 cm⁻¹ matches with the previous report of α -Co(OH)₂, and the shoulder peak at 253 cm⁻¹ suggests the 4-coordinated Co sites from α -Co(OH)₂.⁴⁰ Such peaks indicate the formation of α -Co(OH)₂ after immersing ZIF-67 into the electrolyte. As the applied potential rises from 0.925 to 0.985 V, a new peak develops at 506 cm⁻¹, close to the A_{2u} vibration peak of β -Co(OH)₂, declaring its formation. At 1.045 V, the electrooxidation of Co²⁺ to CoOOH starts, and the low crystallinity of CoOOH is suggested by its broad A_{1g} peak at *ca.* 571 cm⁻¹. This lack of local crystallinity makes it impossible to differentiate the CoOOH species produced by α - and β -Co(OH)₂. Interestingly, the traits of ZIF-67 remain without significant loss of peak intensity, which im-

plies the formation of α/β -Co(OH)₂ and their corresponding CoOOH forms are mainly limited on the surface of ZIF-67. Increasing potential to 1.225 V leads to the rapid decline of ZIF-67 peaks and the rise of CoOOH A_{1g} peak at 571 cm⁻¹, while the broad peaks between 450 and 650 cm⁻¹ reveal the extensive formation of Co(OH)₂ (both α and β phase). No ZIF-67 structure is detected by Raman scattering above 1.285 V, and the dominating peak at 571 cm⁻¹ indicates the conversion of most Co species to CoOOH. Meanwhile, minor peaks (470 and 670 cm⁻¹ at 1.285 and 1.525 V, respectively) are observed, matching the E_g and A_{1g} modes of Co₃O₄.⁴¹ However, as no Co₃O₄ structure is observed by XRD nor XPS, it is likely due to the phase transition of CoOOH/Co(OH)₂ to Co₃O₄ by laser heating (a higher laser power of 5.0 mW leads to full conversion to Co₃O₄ as shown in **Figure S8**).⁴² The reverse scan (**Figure S7D**) shows the incomplete reduction of CoOOH to Co(OH)₂ as indicated by the intense A_{2u} peak at 504 cm⁻¹, which echoes the CV results that the Co³⁺ species are not sufficiently reduced and less active Co²⁺ species (β -Co(OH)₂) is produced. It is thus clear that the previously mentioned Co²⁺[I] and Co²⁺[II] are α - and β -Co(OH)₂, respectively.

Based on the *in situ* and *ex situ* studies, the evolution of the Co sites in ZIF-67 during CV pre-catalytic treatments is proposed as follows:



After exposing ZIF-67 to the alkaline electrolyte (**Figure 4E**), the hydroxide ions would replace the mIM molecules of the tetrahedral Co sites on the surface layer of ZIF-67 to form Co(mIM)₃OH, Co(mIM)₂(OH)₂, Co(mIM)(OH)₃, and eventual Co(OH)₄²⁻ (α -Co(OH)₂). As a result of CV treatment, the capacitive adsorption of OH⁻ further assists such replacements to the inner layers. Meanwhile, the phase transition from α -Co(OH)₂ to β -Co(OH)₂ occurs.⁴³ During Co²⁺ to Co³⁺ electrooxidation, both α - and β -Co(OH)₂ (assigned to previous Co²⁺[I] and Co²⁺[II] species) are converted to their corresponding CoOOH (denoted as CoOOH[I] and CoOOH[II]). Despite its instability, the α phase sites are 9.8 times more active (TOF = 0.59 s⁻¹) compared to the β phase sites (TOF = 0.06 s⁻¹).

Regarding the structure of the CoOOH[I] and CoOOH[II], it is worth emphasizing that a few reports suggested that the electrooxidation products of α -Co(OH)₂ and β -Co(OH)₂ are γ -CoOOH and β -CoOOH respectively, which is yet to be verified by others.^{27, 44} Moreover, the assignment of CoOOH[I] and CoOOH[II] cannot be done based on our spectral evidence due to the poor signal-to-noise ratio of *in situ* experiment and the overlapping signals from Co(OH)₂ and ZIF-67. Therefore, it is reasonable for us to only show the existence of two types of CoOOH here without discussing their detailed structure.

2.5 Amperometric treatment of ZIF-67. The amperometric study is another standard electrochemical method often used to evaluate the electrocatalytic stability of materials at a certain potential. Similar to CV, the amperometric treatment also involves multiple processes driven by the applied potential. In amperometry, however, a fixed potential is applied while the current signal is recorded. At a given potential,

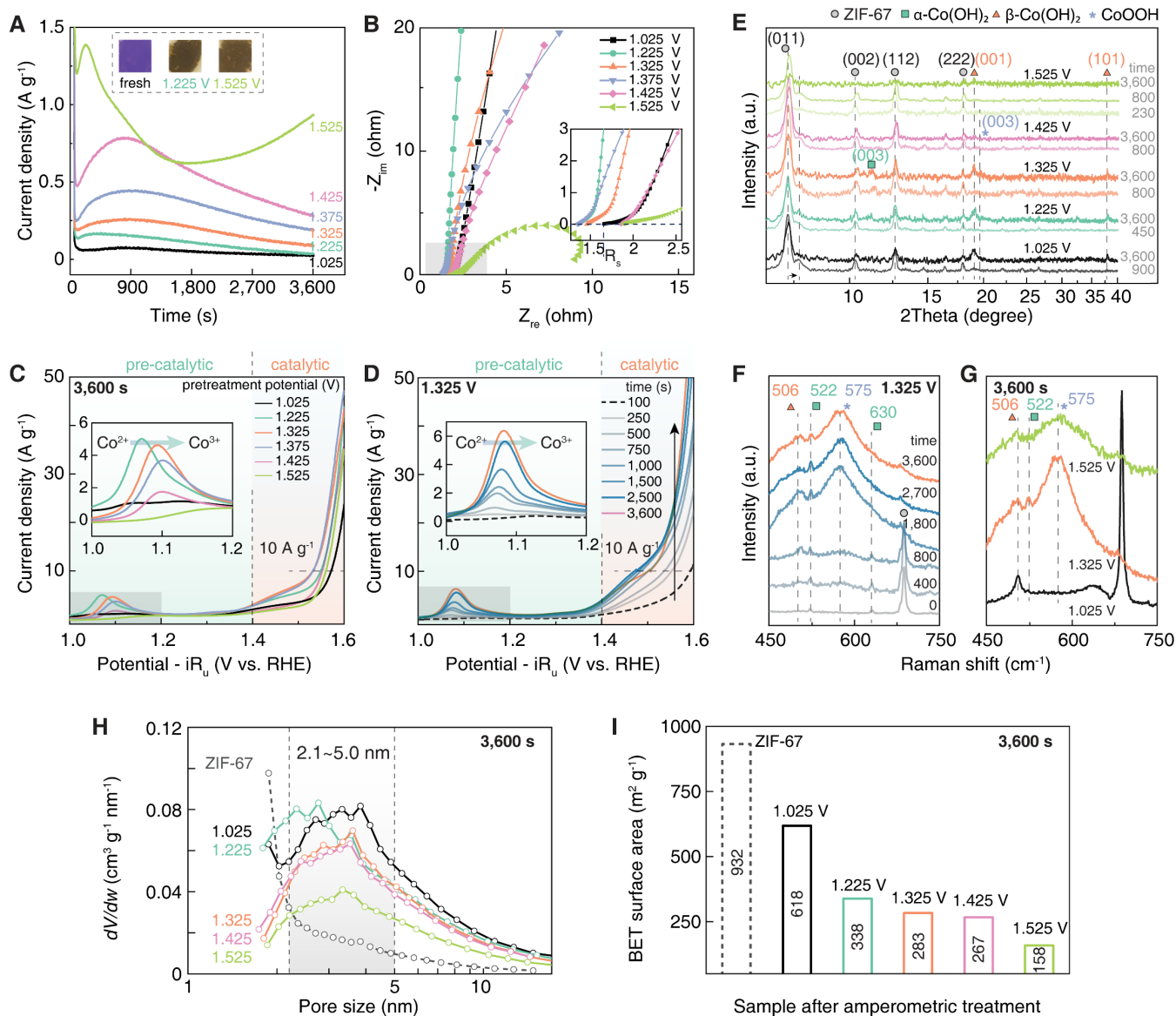


Figure 5. Amperometric treatment of ZIF-67@CFP electrode and the electrochemical properties of treated samples and the structural characterization. **(A)** Amperometric plots of the ZIF-67@CFP electrode at selected applied potentials in 1.0 M KOH electrolyte. Insets are the digital images of the electrode surface before and after treatments (colorless indium tin oxide (ITO) electrodes are used for photo taking). **(B)** Nyquist plots and **(C)** polarization curves of the ZIF-67@CFP electrode after amperometric treatment at selected applied potentials for 1 h. **(D)** Polarization curves of the ZIF@CFP electrode obtained after amperometric treatment at 1.325 V after different duration. **(E)** XRD patterns of ZIF-67 after amperometric treatment at various potentials and time. **(F)** *In situ* Raman spectra of ZIF-67 at different duration during the amperometric treatment at 1.325 V. **(G)** *In situ* Raman spectra of ZIF-67 after 1 h of amperometric treatment at 1.025, 1.325, and 1.525 V. **(H)** Pore size distribution plots and **(I)** BET surface area of pristine ZIF-67 and ZIF-67 samples treated by amperometry at different potentials for 1 h.

amperometry allows us to accumulate redox products while monitoring the electron exchange rate.

Figure 5A shows the amperometric plots of ZIF-67. With applied potentials lower than 1.525 V, the current rises until *ca.* 800 s after the initial drop of non-Faradic current (charging current) within *ca.* 10 s, and declines between 800 and 3,600 s. At 1.025 V, the current increment from 0.060 to 0.078 A g⁻¹ at 900 s indicates the slightly enlarged ECSA, possibly due to the mass transfer of OH⁻ into the pores of ZIF-67 since no Faradic current is expected. Meanwhile, the replacement of mIM linkers by OH⁻ converts ZIF-67 to α - and β -Co(OH)₂, which have a poorer porosity than ZIF-67, explaining the current decline to 0.023 A g⁻¹ after 3,600 s. Once the onset potential of Co²⁺

electrooxidation is reached (*i.e.*, $E \geq 1.325$ V), the Faradic current dominates as a higher potential showing a higher kinetic rate. Because the current is controlled by the concentration gradient of accessible Co²⁺ and OH⁻, the diffusion of OH⁻ and the formation of Co(OH)₂ benefit the accessible Co²⁺ concentration, leading to the current increase until 800 s. After reaching the highest gradient, the produced CoOOH dominates the surface, surpassing Co²⁺ species and causing the current to decline. Further increasing potential to 1.525 V leads to Co²⁺-Co³⁺-Co⁴⁺ electrooxidation. The clear indication of OER current boost is evident from 1,800 s, and the previous Co²⁺-Co³⁺-Co⁴⁺ process can be regarded as the ‘activation’ process since both Co³⁺ and Co⁴⁺ are regarded as the real active sites.²⁰

After the amperometric treatment for 1 h, the samples demonstrate diverse ion transport rates and OER activities as shown by the Nyquist plots and polarization curves (**Figures 5B** and **5C**). Below 1.425 V, all electrodes show excellent ion transports as indicated by the phase angles larger than 45°. The amperometric treatment at 1.525 V renders a depressed semicircular arc, an indication of a single-step charge transfer reaction (Co³⁺ to Co⁴⁺ electrooxidation), yet the smaller phase angle of samples treated at 1.525 V for 1h indicates the decreased ECSA. Meanwhile, the non-compensated resistance (R_s) obtained from the high-frequency region (inset of **Figure 5B**) reveals the conductivity of the modified electrode since the electrolyte resistance is the same for all. The difference in R_s is determined by the conductivity of the electrocatalyst layer as well as the contact resistance between CFP and the electrocatalyst.⁴⁵ The sample treated at 1.225 - 1.375 V shows a lower resistance of *ca.* 1.4 Ω compared to 1.6 Ω (1.025 V) and 1.9 Ω (1.425 and 1.525 V) of the others. The most reasonable explanation is that the formation of CoOOH can reduce the non-compensated resistance while the production of Co⁴⁺ species either decreases the conductivity or undermines the contact of the electrode/catalyst interface.

Depending on the pretreatment potential, significantly different OER performance is achieved. As indicated by the inset of **Figure 5C**, after iR compensation, the pre-catalytic treatment at 1.025 V produces minor accessible Co²⁺ species, while those at 1.225, 1.325, and 1.375 V result in the dramatically increased Co²⁺ populations (Co(OH)₂). The peak shifting of Co²⁺-Co³⁺ oxidation potential after pretreatment at 1.225 and 1.325 V suggests the involvement of more than one Co²⁺ species (suggested below by *in situ* Raman spectra as α/β -Co(OH)₂ in **Figure 5G**, section 2.6) and their potential-dependent content.

Higher pretreatment potential (>1.325 V) leads to major Co²⁺ to Co³⁺ oxidation before the polarization tests, leaving a smaller amount of Co²⁺ to form the oxidation peak during the pre-catalytic region of OER polarization curve. **Figure 5C** shows that the subsequent OER overpotential at 10 A g⁻¹ decreases from 341 mV (pretreated at 1.025 V) to 300 mV (pretreated at 1.325 V) with Tafel slope (**Figure S9**) increasing from 78.6 to 99.4 mV dec⁻¹. The trend of Tafel slope indicates, despite low total numbers, the Co²⁺ sites produced by amperometric treatment at 1.025 V (most likely tetrahedral α -Co(OH)₂ sites) have the highest activity towards OER after pre-catalytic activation. After treatment at a higher potential of 1.325 V, the large population of Co²⁺ sites (β -Co(OH)₂ sites) compensates the lower activity of the individual site. As the pretreatment potential rises to 1.425 and 1.525 V, most Co²⁺ sites have been already oxidized to their Co³⁺ form (CoOOH), showing higher site activity as indicated by the low Tafel slope of 70 mV dec⁻¹ (**Figure S9**), however, as well as higher overpotential (330 mV) due to the decreased total site numbers suggested by the smaller ECSA (**Figure 5B**).

To refine the correlation between amperometric treatment and OER activity, the OER tests are performed using the ZIF-67@CFP electrode pre-treated at 1.325 V for different duration (**Figure 5D**). From 100 to 3,600 s, as shown in the pre-catalytic region, more Co²⁺ sites are exposed for the electrooxidation to Co³⁺. However, the TOF (overpotential = 300 mV) maintains at *ca.* 0.24 s⁻¹ with pretreatment time between 100 and 1,000 s, but drops to 0.13 s⁻¹ and 0.043 s⁻¹ after pretreatment for 1,500 s and 3,600 s, respectively. Therefore, despite

increased site number, the single-site activity of Co drops by 82%. The joint influence of OER performance by the two counterparts is well reflected by the volcano-shaped overpotential trend, which decreases from 362 mV (100 s) to 239 mV (2,500 s) and rises to 293 mV (3,600 s). The reasonable explanation is that, at a short duration (100 - 1000 s), only a small amount of high active Co sites are produced (identified as α -Co(OH)₂ in **Figure 5F**, section 2.6), leading to high TOF yet high overpotential due to the limited number. Prolonged durations, in contrast, produce sufficient sites, but mainly in the low active form (β -Co(OH)₂). Only optimal duration (1000 s - 2500 s) can offer an acceptable site population while maintains mainly the α -Co(OH)₂ form.

2.6 Structural and morphologic evolution of ZIF-67 during amperometry. XRD and *in situ* Raman spectroscopy are engaged to verify the structure degradation of ZIF-67 during amperometric pretreatment. XRD plots in **Figure 5E** reveal the deformation of ZIF-67 suggested by the shoulder peak at 7.7° besides its (011) peak. Below 1.425 V, the co-existence of β -Co(OH)₂ and ZIF-67 are widely observed, along with the minor peak of CoOOH (003) plane if treated between 1.225 and 1.425 V. After OER occurs at 1.525 V, only the peak of ZIF-67 (011) plane is observed with a small indication of (001) peak from β -Co(OH)₂. The broadening of β -Co(OH)₂ peak and disappearance of CoOOH peak at 1.525 V are due to the decreased crystallite size beyond the XRD detection limit. Most interestingly, when treated at 1.325 V, the diffraction peak at 11.7° corresponding to the (003) facet of α -Co(OH)₂ arises,⁴³ while no β -Co(OH)₂ peaks are observed at 800 s. β -Co(OH)₂ only appears at a longer time of 3,600 s. In conjunction with **Figure 5D**, it is clear that Co³⁺ species produced from α -Co(OH)₂ is more active than Co³⁺ species from β -Co(OH)₂. The findings from *in situ* Raman spectra (**Figure 5F**) also support this argument since the vibration bands at 522 and 630 cm⁻² are exclusively assigned to α -Co(OH)₂. **Figure 5G** compares the spectra obtained after 1h treatment at 1.025 V (only capacitive behavior), 1.325 V (electrooxidation of Co²⁺ to Co³⁺), and 1.525 V (dominated by OER), showing that only the treatment at 1.325 V leads to the detectable production of α -Co(OH)₂.

Figures 5H and **5I** compare the pore size distribution and Brunauer-Emmett-Teller (BET) surface area of pristine ZIF-67 and ZIF-67 samples treated by amperometry at different potentials for 1h. The sub-2 nm pore observed from the pristine sample matches well with the theoretical 1.7 nm pore (**Figure 1A**). After amperometric treatments at 1.025 and 1.225 V, the population of the sub-2 nm pores drops rapidly, while new pore structure(s) with diameters of 2.1 ~ 5.0 nm forms, which echoes the destruction of ZIF-67 structure and the formation of porous α/β -Co(OH)₂. Further increased amperometric potentials (1.325 and 1.425 V) lead to minor sub-2 nm pores and dominating larger pores between 2.1 and 5.0 nm, marking the established α/β -Co(OH)₂ structure. As the potential reaches 1.525 V, the population of the pores with diameters of 2.1 ~ 5.0 nm drops, possibly caused by further electrooxidation of α/β -Co(OH)₂ structure. Meanwhile, the BET surface area of ZIF-67 declines dramatically during amperometry, from 932 m² g⁻¹ to 158 m² g⁻¹ after 1h treatment at 1.525 V.

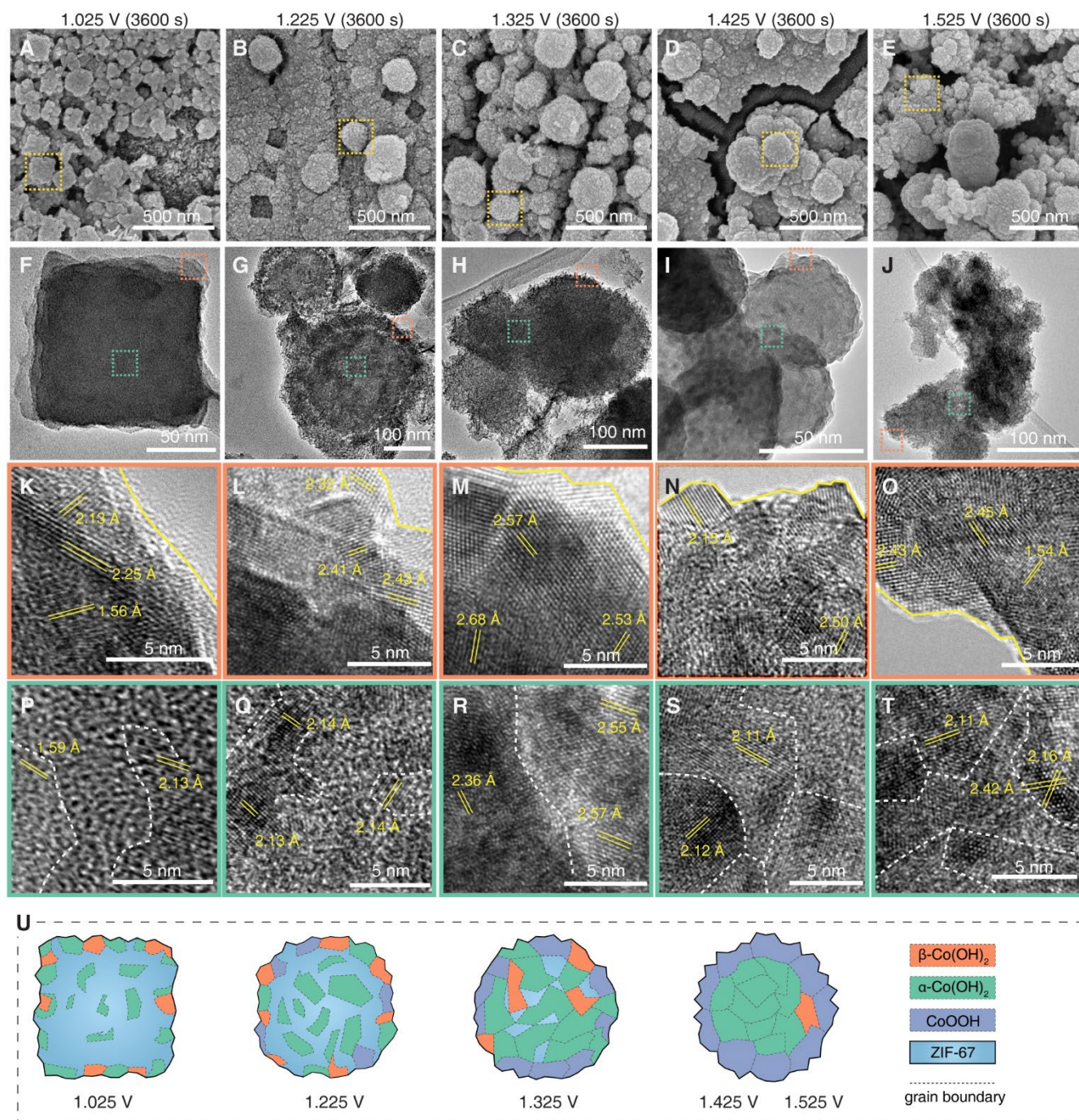


Figure 6. Morphology of ZIF-67@CFP electrode after amperometric study. (A-E) SEM and (F-J) TEM images of ZIF-67 after amperometric treatment at various applied potentials for 1h. (K-T) TEM images of the (K-O) edge (marked in red) and (P-T) center (marked in blue) regions of the corresponding TEM image. The lattice spacings and grain boundaries are illustrated in yellow and dotted lines, respectively. (U) Illustration of the structural evolution of electrocatalyst after amperometric study at the different potential values.

Figure 6 shows the morphologic evolution of ZIF-67 (zoom-out images shown in **Figure S10**). Again, no observable electron damage is evident during the imaging process. Despite the interference from lattice disorder, the interplanar spacing (d spacing) can provide insights towards the formed structures. At 1.025 V, polycrystalline structures appear on both edge and bulk regions of deformed ZIF-67 nanocubes. The d spacings of *ca.* 1.59 and 2.13 Å can be ascribed to the (110) and (018) planes of α -Co(OH)₂, respectively.⁴⁶ The presence of β -Co(OH)₂ is also suggested by the d spacing of 2.25 Å, matching the (101) plane. Therefore, both α and β phases of

Co(OH)₂ co-exist on the surface of the deformed ZIF-67 while the α phase dominates the bulk material, decorated in the ZIF-67 matrix. The α -to- β phase transition only occurs on the surface region since only the surface α -Co(OH)₂ is in direct contact with sufficient hydroxide ions which is essential for a phase transition.⁴⁰ At a higher treatment potential of 1.225 V, no cubic particles are evident. Instead, aggregated spherical particles are formed and the cubic vacancies left by the detached ZIF-67 particles are visible. Clear grain boundaries with d spacings of *ca.* 2.43 and 2.32 Å are shown in the edge region, which are attributed to the (101) plane of CoOOH and

(101) plane of β -Co(OH)₂, respectively, suggesting the surface covered by CoOOH and Co(OH)₂. However, the center region only shows the d spacing of 2.14 Å, indicating the extensive presence of α -Co(OH)₂. The higher amperometric potential at 1.325 V leads to the wide formation of well-defined α -Co(OH)₂ nanocrystal with d spacing of *ca.* 2.68 Å ((100) plane)⁴⁷ on the surface as well as CoOOH (possibly α phase with the d spacing of 2.57 Å). Further raising the potential to 1.425 and 1.525 V results in the spherical nanoparticles with cracks and pores. At 1.525 V, polycrystalline structures are observed with mainly CoOOH on the surface (d spacing of 2.43 Å ascribed to (101) plane),⁴⁸ while the bulk particles still show the presence of α -Co(OH)₂.

3. CONCLUSION

In summary, ZIF-67, as a widely employed example of the MOFs in recent electrochemical applications, is unstable during two common electrochemical studies: CV and amperometry. The real active sites for OER are the intermediated generated by electrochemistry, not the metal nodes.

CV treatment brings a dramatic and irreversible morphologic change to ZIF-67 from cube to the irregular sphere within merely 15 cycles. Even within potential window lower than the redox potential (at $E < E_{\text{Co}^{2+}/\text{Co}^{3+}}$), the sweeping potential sabotages the tetrahedral Co²⁺-organic linker coordination and reveals the electron-accessible Co²⁺ species with increasing cycle number. *In situ* UV-Vis and Raman spectra of the first cycle, as well as *ex situ* characterizations (XRD and XPS), suggest the rapid replacement of the coordinated organic linkers by OH⁻, forming tetrahedral α -Co(OH)₂ followed by the phase transition to its octahedral β phase. At the higher potential during the forward scan (at $E > E_{\text{Co}^{2+}/\text{Co}^{3+}}$), the exposed Co²⁺ sites are further oxidized to their high-valent forms (γ -CoOOH and β -CoOOH), acting as the real active sites for OER, demonstrating the OER TOF of 0.59 s⁻¹ and 0.06 s⁻¹ at an overpotential of 296 mV, respectively. The reverse scan can partially reduce CoOOH to Co(OH)₂, but cannot restore the Co²⁺-organic linker coordination.

Amperometric treatment at selected applied potentials also reveals the electrochemical instability of ZIF-67. Rapid morphologic and structural changes happen within 900 s, producing mainly α -Co(OH)₂ in the bulk and polycrystalline structure of α/β -Co(OH)₂ as well as CoOOH (at $E > E_{\text{Co}^{2+}/\text{Co}^{3+}}$) on the surface. Higher potential and longer amperometric treatments result in more Co²⁺ exposure but also the conversion of α -Co(OH)₂ to its less active β phase. Consequently, the *in situ* produced hybrid α/β -Co(OH)₂ species (and their oxidized forms of Co³⁺ and Co⁴⁺) on the surface of ZIF-67 during the electrochemical test are the dominating active sites for OER, other than the instable Co nodes of ZIF-67. The overall performance (overpotential) is controlled by the total number of Co sites and the relative contents of CoOOH produced by α/β -Co(OH)₂.

On the comprehensive demonstration of the electrochemical instability of ZIF-67, we have confirmed that both CV and amperometric characterizations are destructive methods for MOFs study. In alkaline electrolyte, the sweeping potential during CV can result in a relatively fast destruction of ZIF-67 and the formation of Co(OH)₂/CoOOH, due to the dynamical electrochemical double layer driven by potential. Differently, the fixed potential during amperometry forms a relatively stable double-layer structure, in which the replacement of coor-

dated organic linkers by OH⁻ occurs from surface to bulk MOF, as well as the electrooxidation from Co(OH)₂ to CoOOH.

Therefore, the information acquired from electrochemical methods may not provide genuine insights towards the real properties of MOFs, other than the intermediates produced chemically and electrochemically. Similarly, the catalytic findings from electrochemistry cannot be attributed to MOFs automatically without careful study of the actual journey of the MOFs. In future MOFs studies, especially those that directly use MOFs as electrocatalysts, it is needed to examine the structure during and after electrochemical and electrocatalytic studies to ensure the role of MOFs and guide appropriate electrocatalyst design.

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Author Contributions

WZ designed the experiments, conducted the electrochemical experiments (CV, EIS, and *in situ* UV-Vis SPECE) as well as data analysis and visualization. ML performed the *in situ* Raman SPECE, XRD, XPS, FESEM and TEM. LL supervised the progress of this project and drafted the manuscript with WZ.

§these authors contributed equally to this work.

Notes

The authors declare no conflict of interest.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The synthesis of ZIF-67, characterization methods, electrochemical characterization details, TOF calculation, Nyquist plots, Examples of CV curve fitting, Tafel plots; XPS spectra, SEM images, *in situ* spectroelectrochemical experiment setup and the reverse scan, and Laser intensity study.

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1 *ligand substitution* 2 *phase transition*

