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# Discrimination of the key single-atom electrocatalysis in MOFderived bifunctional catalysts

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#### Hangrong Chen\*<sup>[a]</sup>

Abstract: Metal-organic frameworks (MOFs)-derived materials have attracted increasing interests, which show promising catalytic performances in many fields. Intensive efforts have been focused on the structure design and metal-site integration in MOF-derived catalysts. However, the key catalytic processes related with the metal sites in MOF-derived catalysts which dominate the electrocatalytic performance still remains obscure. Herein, we show a neglected while critical issue in the pyrolytic synthesis of MOFderived catalysts: the coupled evolution of dual sites, i.e., metallic sites and single-atom metal sites. The identification of active sites of single-atom sites from the visible particles is elucidated through the combined X-ray spectroscopic, electron microscopic, and electrochemical studies. Interestingly, after a total removal of metallic cobalt sites, catalysts with purified single-atom metal sites show no activity falter for either oxygen reduction reaction (ORR) or hydrogen evolution reaction (HER), while significantly enhanced ORR selectivity is achieved, revealing the dominant activity and selectivity contribution from single-atom electrocatalysis. The insight of the coupled evolution of dual sites and the as-demonstrated dual sites decoupling strategies open up a new routine for the design and synthesis of MOF-derived catalysts with the optimized single-atom electrocatalysis towards various electrochemical reactions.

#### Introduction

With the rapid consumption of fossil energy, the energy crisis and environment pollution have gradually attracted wide concerns, which stimulates intensive efforts focused on the exploitation of the clean energy conversion and storage devices, such as fuel cells <sup>[1]</sup>, and metal-air batteries <sup>[2]</sup>, and electrolyzers <sup>[3]</sup>. As two of the critical reactions which control the performance of these devices, oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER), however, are kinetically sluggish <sup>[4]</sup>. Currently, platinum (Pt)-based catalysts benchmark the ORR and HER activities <sup>[5]</sup>. To make these devices to be commercially visible, considerable efforts have been devoted on the development of noble-metal-free catalysts, such as transition metal oxides/sulfide/phosphides <sup>[6]</sup>, molecular complexes of transition metal species <sup>[7]</sup>, and heterogeneous carbon materials

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<sup>[8]</sup>. Among them, nitrogen-doped carbons with an integration of transition metal sites show the promising electrocatalytic activities for both ORR and HER, especially in the harsh acid <sup>[9]</sup>. As evidenced by several pioneering studies, high ORR activities in acid were observed after a high-temperature pyrolysis of metal and nitrogen-containing precursors with supports <sup>[10]</sup>. And the introduction of the metal sites in the obtained catalysts was found to have key effects on promoting the catalytic activity <sup>[9a, 9b]</sup>.

The activity of the traditional catalysts is often attributed to the surface metal sites in the supported-particles. Until recently, the atomically dispersed metal sites from the support-assisted pyrolytic synthesis are found to be another type of active sites, and therefore opening a new research frontier of single-atom electrocatalysis towards substituting Pt for efficient ORR and HER catalysis <sup>[11]</sup>.

In previous studies, the synthesis of active catalysts is often involved in a support-assisted pyrolysis of metal-organic complexes. Recently, metal-organic frameworks (MOFs) with high surface area, well-engineered porous structure, and multimetal coordination sites, e.g., zeolitic imidazolate framework (ZIF) <sup>[12]</sup>, are demonstrated to be an ideal host for the construction of catalytic metal sites through pyrolysis without additional supports.<sup>[13]</sup> For instance, Eric et al showed the achievement of a higher power density using MOF templates.<sup>[14]</sup> And the development of MOF as ORR catalysts is also reported by Liu's and Jiang's group.<sup>[15]</sup> Besides ORR catalysis, many MOF-derived catalysts have also attracted wide interests for other electrocatalysis reactions and organic synthesis.<sup>[16]</sup> Nevertheless, there is still a controversy over the roles of different metal sites. For example, in some MOF-derived catalysts, the metal sites are found to be in the forms of metallic nanoparticles which are encapsulated by nitrogen doped graphite shells (labeled as M@C or a more precise M@C-N) <sup>[17]</sup>. While Jaouen and Li et al reported that the electrocatalytic activities resulted from the single-atom (SA) metal sites <sup>[18]</sup>. And some other studies suggested the possible synergetic effects from both dual sites construction [19]. Therefore, advance towards further progresses on MOF-derived catalysts requires better insights into the dual sites evolution and the role of singleatom electrocatalysis.

Herein, we show a coupled evolution of both single-atom cobalt sites and Co@C-N sites in the pyrolysis of Zn/Co bimetallic metal-organic frameworks (ZnCo-biMOF), which is confirmed by the advanced X-ray spectroscopic and electron microscopic characterizations. It is futher demonstrated that a removal of the metallic particles through a sulfur-assisted sites purification strategy induces no decline for both ORR and HER activities, indicating the main catalytic contribution from the atomic cobalt sites. More importantly, a favorable four-electron catalytic pathway is achieved for catalysts dominated with single-atom cobalt sites, showing the key effects of single-atom electrocataysis for enhanced adsorption of ORR intermediates. Accordingly, the optimized catalysts exhibit superior ORR and HER performances, approaching to that of the commercial 20%

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Pt/C catalyst under the same condition. Our studies show the key activity and selectivity contributions from single-atom electrocatalysis in MOF-derived catalysts, paving a new direction for future noble-metal-free electrocatalysts design.

#### **Results and Discussion**

The catalysts synthesis involves a pyrolysis of ZnCo-biMOF with or without adsorbing the DMSO into the MOF cavity, following by a pyrolysis of 900 $^{\circ}$ C for 2h and acid etching (Figure 1), and the



Figure 1. Illustration of the coupled evolution of single-atom cobalt sites and metallic cobalt sites and their decoupling process

resulting catalysts are labeled as Co-SAC and Py-ZIF, respectively. Additionally, two reference catalysts S-NC and NC containing no Co species were also synthesized for comparison through a pyrolysis of ZIF-8 with or without sulfur species, respectively. The X-ray diffraction (XRD) was used to analyze the composition of the prepared catalysts. As shown in Figure S1, the XRD pattern of ZnCo-biMOF confirms its high crystallinity with similar zeolite-type structure. After pyrolysis and acid etch, catalyst Py-ZIF shows the existence of metallic cobalt, which, however, is clearly absent in the catalyst Co-SAC from a sulfur-assisted pyrolysis (Figure 2a). The broad peak at 26.5°, attributed to the (0 0 2) plane of graphitic carbon, is observed in both catalysts. As compared to that of catalyst Co-SAC, there is a generation of cobalt particles and carbon nanotubes in catalyst Py-ZIF (Figure 3c). Compared with catalyst Co-SAC, the higher graphitization degree and specific surface areas in catalyst Py-ZIF is obtained, as demonstrated by the lower  $I_D/I_G$  value from Raman spectra measurement (Figure S4) and higher Brunauer-Emmett-Teller (BET) surface area (Figure 2b), respectively. The high BET surface areas of catalysts are helpful to the exposure of active sites and the diffusion of the related species.

The surface elemental composition and chemical state of the catalysts were investigated by the X-ray photoelectron spectroscopy (XPS) measurement. The survey scan spectrum shows the co-presence of cobalt, carbon, nitrogen and oxygen species in catalysts Py-ZIF and Co-SAC (Figure S5). No Zn elements are detected because of the volatilization of Zn species during the pyrolysis <sup>[20]</sup>. And the corresponding high-resolution



**Figure 2.** Typical structural characterization of different catalysts. The XRD (a) patterns and N<sub>2</sub> sorption isotherms (b) of different catalysts. High resolution N 1s XPS of nitrogen for catalysts Py-ZIF (c) and Co-SAC (d). The XANES (e) and *k*<sup>2</sup>-weighed Fourier transform of the EXAFS (f) for catalysts Py-ZIF, and Co-SAC with cobalt phthalocyanine (CoPc) and cobalt foil as reference.

N1s spectrum can be divided into three peaks at 398.6, 400.1 and 401.1 eV, assignable to the Pyridinic N, Pyrrolic N, and Graphitic N, respectively (Figure 2c and 2d). Both Py-ZIF and Co-SAC have a high proportion of pyridinic N and pyrrolic N, which have been demonstrated to be able to stabilize the atomic cobalt sites due to the coordination effect [21]. It is worth noting that there is an obvious reduction of cobalt contents in catalyst Co-SAC (Figure S6, Table S1 and S2), which is attributed to the efficient removal of cobalt particles during sulfur-assisted pyrolysis process. The chemical environment around cobalt centers in Py-ZIF and Co-SAC is further probed by the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at Co K-edge(Figure 2e, 2f). It is clearly found that the XANES feature of catalyst Py-ZIF is more close to that of Co foil, indicative of the dominating form of metallic Co in Py-ZIF. While, catalyst Co-SAC shows the similar edge energy position to CoPc with molecular structure. The evolution of different peaks in the Fourier transformed-(FT) EXAFS represents varied cobalt coordination environments: Co-N/O bonding located at 1.3-1.5 Å and Co-Co bonding located at 2.1. As shown in Figure 3f, Py-ZIF contains both a strong Co-Co bonding and an obvious Co-N/O bonding. In contrast, there is dominating Co-N bonding in catalyst Co-SAC with the absence of Co-Co bonding, indicating the evolution of the atomically dispersed cobalt sites. The EXAFS fitting results further reveal the average nitrogen coordination number of 4 around cobalt species, suggesting that the SA-Co sites are stabilized by four nitrogen atoms in the resultant carbon (Figure S7).



**Figure 3.** Morphology and compositions characterization of catalysts. The SEM (a), STEM and the corresponding element mapping (b), TEM (c) and HAADF-STEM (d) images of Py-ZIF. The SEM (e), STEM and the elemental mapping (f), TEM (g) and HAADF-STEM (h) images of Co-SAC.

The above results indicate that both SA-Co and Co@C-N sites are coupled to occur in catalyst Py-ZIF through a simple pyrolysis of MOF, while Co-SAC catalyst only possess the SA-Co sites, which implies that the sulfur-assisted pyrolysis strategy can effectively decouple the dual sites of Co@C-N and SA-Co, obtaining the cobalt-centered single-atom catalyst. The role of sulfur species is believed to interact with cobalt species to form CoS<sub>x</sub> species, preventing the formation of encased metallic particles within graphite layers at high temperature <sup>[22]</sup>. Afterwards, CoS<sub>x</sub> species are subjected to the acid etching, and the SA-Co sites can be stabilized by the coordinative nitroge. The coupled evolution and the successful dual-sites decoupling could be directly observed by the scanning electron microscope (SEM) and transmission electron microscope (TEM).

As shown in TEM images (Figure S2), a uniform polyhedronlike ZnCo-biMOF was firstly obtained. After pyrolysis and acid etching, the resulting catalyst Py-ZIF keeps the overall polyhedron-like morphology of parent ZnCo-biMOF, and clearly shows abundant of metallic cobalt nanoparticles which are encased in the carbon nanotubes (Figure 3a and Figure 3c). The corresponding elemental mapping confirms the Co signals are concentrated on the Co particles, while N is uniformly distributed (Figure 3b). Catalyst Py-ZIF shows obvious cobalt-based nanoparticles in the high-angle annular dark-field scanning transmission electron microscope (HADDF-STEM) image (Figure 3d), while, no Co nanoparticles can be found in the catalyst Co-SAC obtained via sulfur-assisted pyrolysis (Figure 3e, 3g and S3). The corresponding elemental mapping clearly shows the uniform distribution of Co and N elements (Figure 3f), further confirming the evolution of well-dispersed SA-Co sites in the catalyst Co-SAC (Figure 3h). The above results indicate that both SA-Co and Co@C-N sites are coupled to occur in catalyst Py-ZIF in the pyrolysis of MOF, while the formation of cobalt nanoparticles can greatly be inhibited during the sulfur-assisted pyrolysis of MOF under the same condition, obtaining the purification of SA-Co sites.

The ORR and HER performances of catalysts with the coupled dual sites and decoupled SA-Co sites were further investigated by steady-state linear sweep voltammetry (LSV) measurement. As indicated by the low onset potential (Eonset, Figure 4a), both two references cobalt-free catalyst NC and S-NC show poor ORR activity, indicating that the introduction of cobalt species is much beneficial to enhance ORR performance in alkaline medium. Catalysts Py-ZIF and Co-SAC exhibit a similar Eonset around 0.99 V (vs. RHE) and half-wave potential (E1/2) around 0.84 V (vs. RHE), comparable with that of the benchmark Pt/C catalyst (Eonset = 0.96V, E1/2 = 0.83V). And the Tafel slopes of Py-ZIF and Co-SAC are 78 mV dec-1 and 83 mV dec<sup>-1</sup>, respectively, lower than that of Pt/C (88 mV dec<sup>-1</sup>, Figure S8a). The rotating ring disk electrode (RRDE) tests were conducted to investigate the ORR pathways of the catalysts. As shown in Figure 4b, the electron-transfer number (n) of Py-ZIF is about 3.82, and the H<sub>2</sub>O<sub>2</sub> yield was calculated to be less than 8.9% in the range from 0.2-0.8 V. Interestingly, Co-SAC shows a higher *n* of 3.89 and a much lower  $H_2O_2$  yield, indicating a better ORR selectivity towards four electron pathway than catalyst Py-ZIF in the alkaline media.

Under acidic medium, cobalt-containing catalysts also show superior performances to those of references NC and S-NC. Both the prepared Co-SAC and Py-ZIF show similar Eonset, E1/2 values and Tafel slopes ( $E_{onset}$  = 0.91V,  $E_{1/2}$  = 0.76V, Figure 4c and S8b), which are close to those of commercial Pt/C catalyst  $(E_{onset} = 0.94V, E_{1/2} = 0.82V)$  and comparable with that of other high performance noble-free catalysts (Table S3), indicating a comparable ORR activity in acidic medium. It is worth noting that Co-SAC presents a much higher ORR selectivity than that of Py-ZIF in acidic medium (n = 3.92, (H<sub>2</sub>O<sub>2</sub>) % = 4.10%), demonstrated by the higher *n* and lower  $H_2O_2$  yield (*n* = 3.97,  $(H_2O_2)$  % = 1.59% Figure 4d), which is very close to the commercial Pt/C catalyst. The above results indicate that the removal of Co@NC sites can not necessarily decrease the overall ORR activities of MOF-derived catalysts, suggesting SA-Co sites are the more active ORR-catalysis sites and could make dominate contributions to the performances, which is distinctive from previous understanding of the catalysts with dual sites presented <sup>[12b, 12c, 23]</sup>. The conclusion of the main catalytic contributions from SA-Co sites was further confirmed by the similar stability performances of catalysts with dual sites and removed metallic cobalt sites (Figure S9, S10 and S11), confirming the key electrocatalytic roles of the atomic metal sites, i.e., as compared to SA-Co sites, there is less important role of Co@C-N sites for ORR catalysis. Additionally, in both acidic and alkaline media, as compared to catalyst NC, the introduction of sulfur doping in catalyst S-NC could not induce significantly activity change. Therefore, instead of the supplementary effects from sulfur doping, the unchanged ORR activity in catalyst Co-

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SAC with removed cobalt particle as compared to catalyst Py-ZIF mainly attribute to the purification of SA-Co sites.

b 6 Pt/ 0.1 M KOF 0.1 M KOF 0.5 E(V vs RHE) 0.6 E(V vs RHE) d С 0.1 M HCIO ć, I,0.(%) 20% Pt/0 <u>j</u> 0.1 M HCIO 0.6 E(V vs RHE) E(V vs RHE) f e - Py-ZIF b=80 mV dec - Co-SAC b=84 mV dec - 20% Pt/C b=34 mV dec сш<sup>-2</sup> N. 0.5 M H.SO 0.5 M H SO E(V vs RHE) log|j, (mA cm<sup>-2</sup>)|

Figure 4. The ORR and HER performances of different catalysts. The LSV curves of catalysts NC. S-NC. Py-ZIF. Co-SAC and 20% Pt/C in oxygensaturated 0.1 M KOH (a), 0.1 M HClO<sub>4</sub> (c) and nitrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> (e). Electron-transfer number (n) and H<sub>2</sub>O<sub>2</sub> yield of different catalysts in oxygen-saturated 0.1 M KOH (b) and 0.1 M HClO<sub>4</sub> (d). (f) The corresponding Tafel slopes of different catalysts in nitrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Notably, as compared to the case of dual sites, there is a higher ORR selectivity in catalysts with the purified SA-Co sites in both acidic and alkaline media, which is believed to mainly relate to the significantly favored adsorption of intermediates (such as H<sub>2</sub>O<sub>2</sub>) on SA-Co sites, rather than Co@C-N sites. Our observations on the different contributions towards H<sub>2</sub>O<sub>2</sub> reduction from Co@C-N and SA-Co sites are consistent with previous Jaouen's conclusion on iron-sites [24].

Similar phenomena can be further demonstrated in HER. Two references cobalt-free catalyst NC and S-NC show poor HER activity in nitrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>, indicated by the low Eonset (Figure 4e). While, both Co-SAC and Py-ZIF exhibit a reduced and similar overpotential of 260 mV at a current density of 10 mA cm<sup>-2</sup>, and the corresponding Tafel slopes of Py-ZIF and Co-SAC are 80 mV dec<sup>-1</sup> and 84 mV dec<sup>-1</sup> (Figure 4f). Similarly, Py-ZIF and Co-SAC also show excellent HER stability, as revealed by no obvious shifts of LSV curves after 2000 cycles and the i-t curves by chronoamperometry at a constant voltage of -0.25V in acid medium (Figure S12 and S13). In brief, both Py-ZIF and Co-SAC have high performances in ORR and HER, approaching to that of the commercial 20% Pt/C catalyst under the same condition. In particular, compared to Py-ZIF, Co-SAC maintains high ORR and HER activities and even better ORR selectivity after a removal of cobalt-based nanoparticles. Therefore, it is believed that the SA-Co sites make dominant activiy and selectivity contributions for both ORR and HER, and more importantly, such SA-Co sites can be selectively generated in the N-doped carbon materials through the sulfur-assisted pyrolysis method.

#### Conclusions

In conclusion, we originally reveal the coupled evolution of dual sites (SA-Co and Co@C-N sites) from a direct pyrolysis of MOF, and then demonstrate the synthetic strategy of sulfur-assisted pyrolysis for dual-sites decoupling and SA-Co sites purification. It is found that catalyst with the total removal of metallic sites shows no ORR and HER activity falters while increased ORR selectivity. It is believed that the single-atom electrocatalysis occurred at the SA-Co sites plays dominate roles in both the ORR and HER processes of MOF-derived catalysts. Besides the main contributions from elucidating single-atom electrocatalysis, this study highlights the significance of SA sites construction and sites purifying for enhancing ORR selectivity, which is much beneficial for promoting the stability issues towards device application. The identification of single-atom electrocatalysis in MOF-derived catalysts, and the methodology of performance optimization through a dual-metal-sites decoupling provide an important guidance towards the rational design of noble-metal-free catalysts for electrochemical reduction of O<sub>2</sub> and CO<sub>2</sub>, and water splitting, and organic synthesis, etc.

#### **Experimental Section**

#### Preparation of ZnCo-biMOF, ZIF-8

For ZnCo-biMOF, 1.8 mmol of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 10.2 mmol of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 120 mL of methanol to form a clear solution, which was subsequently poured into 40 mL of methanol containing 48 mmol of 2- methylimidazole with vigorous stirring. The reaction proceeded for 24 h at room temperature. Then the obtained precipitates were collected by centrifugation, washed with ethanol three times, and finally freeze dried overnight. And sample ZIF-8 was synthesized under the same conditions with 12 mmol of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, instead of 1.8 mmol of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 10.2 mmol of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.

#### Preparation of S-ZnCo-biMOF, S-ZIF-8

0.3 g of the dried ZnCo-biMOF/ ZIF-8 was transferred into 30 mL of a 0.2 M Dimethyl sulfoxide (DMSO) (ethanol solution) with vigorous stirring. After 6 h of reaction at room temperature, the product was separated by centrifugation, washed with ethanol three times, and finally freeze dried overnight.

#### Preparation of Py-ZIF, Co-SAC, NC, S-NC

0.3 g of the dried ZnCo-biMOF/ S-ZnCo-biMOF/ ZIF-8/ S-ZIF-8 was grinded, transferred to a furnace, and heated at 900 °C for 2 h (with a heating rate of 10 °C min-1) under nitrogen flow. After pyrolysis, the obtained samples were immersed in 3 M hydrochloric acid at 80  $^\circ\!\mathrm{C}$  for 6 hours. Then the obtained precipitates were collected by centrifugation, washed with water until neutral, and finally freeze dried overnight.

#### Characterization

The morphology and nanostructures of the samples were characterized by using a JEM-2100F transmission electron microscope (TEM), a



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Maggellan 400 field-emission scanning electron microscope (FESEM) and a FEI Talos microscope operated at 200 kV. The powder X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku D/Max-2550 V diffractometer with Cu K radiation source (40 kV, 40 mA) and a scanning rate of 4° min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) signals were gathered on a VG Micro MK II instrument using monochromatic Mg Ka X-rays at 1253.6 eV operated at 150 W, and spectrum calibration was performed by taking the C 1s electron peak (BE = 285 eV) as internal reference. Raman spectra were performed on a DXR Raman microscope with a 532 nm excitation length (Thermo Nicolet Corporation). Nitrogen adsorption-desorption isotherms were measured using Micromeritics Tristar 3000 at 77k, and the specific surface area were calculated using the BET theory methods. The Co K-edge XANES and EXAFS measurements were carried out at end station 12 BM-B in the fluorescence mode at Advanced Photon Source, Argonne national Laboratory.

#### **Electrochemical measurements**

The ORR performance was tested in O2-saturated 0.1 M HCIO4 or 0.1 M KOH at room temperature on a rotating-disk electrode (RDE) or a rotating Pt-ring-disk electrode (RRDE) system (Pine Inc, GC, d = 5 mm) with a CHI 760E electrochemical workstation (CH Instruments). A carbon stick electrode and an Ag/AgCl electrode (3M KCl) were used as counter electrode and reference electrode, respectively. Catalyst ink was prepared by blending catalyst power (10 mg) with 1 mL of mixed solution (isopropanol: water = 3 : 1, volume scale) and 50 µL Nafion solution (5%) in the ultrasonic bath. The loading of the catalyst was 0.5 mg cm<sup>-2</sup> on the GC disk electrode. Before the electrochemical tests, all the electrodes were activated by potential cycling in acidic media from 1.00 V to 0.10 V for 50 cycles at a scan rate of 50 mV s<sup>-1</sup>. The CV curves in nitrogen- and oxygen-saturated media were collected at a scan rate of 50mV s<sup>-1</sup>. RDE and RRDE measurements were performed at a scan rate of 5 mV s<sup>-1</sup> with rotation rates of 1600 rpm. And the accelerated durability tests in alkaline and acidic media were carried out in O2 saturated 0.1 M HClO4 solution with the potential cyclic between 0.5 V and 1.0 V vs RHE at a scan rate of 50 mV s<sup>-1</sup>. To determine  $H_2O_2$  yield and the number of electrons transferred (n), the ring electrode was held at 1.2 V vs RHE to oxidize H<sub>2</sub>O<sub>2</sub> diffusing from the disk electrode. The electron-transfer number (n) and the percentage of H2O2 released during ORR [(H2O2) %] were calculated by the following equations:

$$n = 4 \times \frac{I_d}{I_d + I_r/N}$$

$$(H_2 O_2) \% = 200 \times \frac{I_r/N}{I_d + I_r/N}$$

in which  $I_d$  is the Faradaic current at the disk,  $I_r$  is the Faradaic current at the ring, and N is the  $H_2O_2$  collection coefficient at the Pt ring. N was determined to be 0.37 from the reduction of  $K_3Fe(CN)_6$ .

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- [1] B. Dunn, H. Kamath, J. M. Tarascon, Science 2011, 334, 928-935.
- [2] Y. C. Lu, B. M. Gallant, D. G. Kwabi, J. R. Harding, R. R. Mitchell, M. S. Whittingham, Y. Shao-Horn, *Energy & Environmental Science* 2013, 6, 750-768.
- [3] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem Rev* 2010, *110*, 6446-6473.
- [4] a) I. Katsounaros, S. Cherevko, A. R. Zeradjanin, K. J. Mayrhofer, Angew Chem Int Ed Engl 2014, 53, 102-121; b) J. K. Norskov, C. H. Christensen, Science 2006, 312, 1322-1323.
- a) N. M. Markovic, T. J. Schmidt, V. Stamenkovic, P. N. Ross, *Fuel Cells* 2001, *1*, 105-116; b) V. R. Stamenkovic, B. S. Mun, M. Arenz, K. J. Mayrhofer, C. A. Lucas, G. Wang, P. N. Ross, N. M. Markovic, *Nat Mater* 2007, *6*, 241-247.
- [6] a) S. Guo, S. Zhang, S. Sun, *Angew Chem Int Ed Engl* **2013**, *52*, 8526-8544; b) T. F. Jaramillo, K. P. Jorgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science* **2007**, *317*, 100-102; c) E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis, R. E. Schaak, *Angew Chem Int Ed Engl* **2014**, *53*, 5427-5430.
- [7] H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long, C. J. Chang, *Science* 2012, 335, 698-702.
- [8] K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, Science 2009, 323, 760-764.
- a) H. Fei, J. Dong, M. J. Arellano-Jimenez, G. Ye, N. Dong Kim, E. L. Samuel, Z. Peng, Z. Zhu, F. Qin, J. Bao, M. J. Yacaman, P. M. Ajayan, D. Chen, J. M. Tour, *Nat Commun* **2015**, *6*, 8668; b) H. W. Liang, S. Bruller, R. Dong, J. Zhang, X. Feng, K. Mullen, *Nat Commun* **2015**, *6*, 7992; c) Y. C. Wang, Y. J. Lai, L. Song, Z. Y. Zhou, J. G. Liu, Q. Wang, X. D. Yang, C. Chen, W. Shi, Y. P. Zheng, M. Rauf, S. G. Sun, *Angew Chem Int Ed Engl* **2015**, *54*, 9907-9910; d) G. Wu, K. L. More, C. M. Johnston, P. Zelenay, *Science* **2011**, *332*, 443-447.
- [10] a) I. Herrmann, U. I. Kramm, S. Fiechter, P. Bogdanoff, *Electrochimica Acta* 2009, *54*, 4275-4287; b) U. I. Kramm, I. Herrmann-Geppert, J. Behrends, K. Lips, S. Fiechter, P. Bogdanoff, *J Am Chem Soc* 2016, 138, 635-640; c) M. Lefevre, E. Proietti, F. Jaouen, J. P. Dodelet, *Science* 2009, 324, 71-74.
- [11] a) W. Liu, L. Cao, W. Cheng, Y. Cao, X. Liu, W. Zhang, X. Mou, L. Jin, X. Zheng, W. Che, Q. Liu, T. Yao, S. Wei, *Angew Chem Int Ed Engl* 2017, 56, 9312-9317; b) W. Liu, L. Zhang, X. Liu, X. Liu, X. Yang, S. Miao, W. Wang, A. Wang, T. Zhang, J Am Chem Soc 2017, 139, 10790-10798; c) W. G. Liu, L. L. Zhang, W. S. Yan, X. Y. Liu, X. F. Yang, S. Miao, W. T. Wang, A. Q. Wang, T. Zhang, *Chemical Science* 2016, 7, 5758-5764; d) M. Zhang, Y. G. Wang, W. Chen, J. Dong, L. Zheng, J. Luo, J. Wan, S. Tian, W. C. Cheong, D. Wang, Y. Li, J Am Chem Soc 2017, 139, 10976-10979.
- [12] a) L. Fan, P. F. Liu, X. Yan, L. Gu, Z. Z. Yang, H. G. Yang, S. Qiu, X. Yao, *Nat Commun* **2016**, *7*, 10667; b) K. Strickland, E. Miner, Q. Jia, U. Tylus, N. Ramaswamy, W. Liang, M. T. Sougrati, F. Jaouen, S. Mukerjee, *Nat Commun* **2015**, *6*, 7343; c) B. You, N. Jiang, M. L. Sheng, W. S. Drisdell, J. Yano, Y. J. Sun, *Acs Catalysis* **2015**, *5*, 7068-7076.
- [13] a) Q.-L. Zhu, W. Xia, L.-R. Zheng, R. Zou, Z. Liu, Q. Xu, *Acs Energy Letters* 2017, 2, 504-511; b) Q.-L. Zhu, W. Xia, T. Akita, R. Zou, Q. Xu, *Advanced Materials* 2016, 28, 6391-+; c) H. Wang, Q.-L. Zhu, R. Zou, Q. Xu, *Chem* 2017, 2, 52-80; d) A. Aijaz, N. Fujiwara, Q. Xu, *Journal of the American Chemical Society* 2014, 136, 6790-6793; e) B. Liu, H. Shioyama, T. Akita, Q. Xu, *Journal of the American Chemical Society* 2018, 130, 5390-+; f) S. Dang, Q.-L. Zhu, Q. Xu, *Nature Reviews Materials* 2018, 3.
- [14] E. Proietti, F. Jaouen, M. Lefevre, N. Larouche, J. Tian, J. Herranz, J. P. Dodelet, *Nature Communications* 2011, 2.
- [15] a) S. Q. Ma, G. A. Goenaga, A. V. Call, D. J. Liu, *Chem.-Eur. J.* 2011, 17, 2063-2067; b) D. Zhao, J.-L. Shui, L. R. Grabstanowicz, C. Chen, S. M. Commet, T. Xu, J. Lu, D.-J. Liu, *Advanced Materials* 2014, *26*, 1093-

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1097; c) Y. Z. Chen, C. M. Wang, Z. Y. Wu, Y. J. Xiong, Q. Xu, S. H. Yu, H. L. Jiang, *Advanced Materials* **2015**, *27*, 5010-5016.

- [16] a) R. V. Jagadeesh, K. Murugesan, A. S. Alshammari, H. Neumann, M.-M. Pohl, J. Radnik, M. Beller, *Science* **2017**; b) W. Ju, A. Bagger, G.-P. Hao, A. S. Varela, I. Sinev, V. Bon, B. Roldan Cuenya, S. Kaskel, J. Rossmeisl, P. Strasser, *Nature Communications* **2017**, *8*, 944; c) A. Morozan, V. Goellner, Y. Nedellec, J. Hannauer, F. Jaouen, *Journal of the Electrochemical Society* **2015**, *162*, H719-H726.
- [17] J. Deng, P. Ren, D. Deng, X. Bao, Angew Chem Int Ed Engl 2015, 54, 2100-2104.
- [18] a) J. K. Li, S. Ghoshal, W. T. Liang, M. T. Sougrati, F. Jaouen, B. Halevi, S. McKinney, G. McCool, C. R. Ma, X. X. Yuan, Z. F. Ma, S. Mukerjee, Q. Y. Jia, *Energy & Environmental Science* **2016**, *9*, 2418-2432; b) A. Zitolo, V. Goellner, V. Armel, M. T. Sougrati, T. Mineva, L. Stievano, E. Fonda, F. Jaouen, *Nat Mater* **2015**, *14*, 937-942.
- [19] W.-J. Jiang, L. Gu, L. Li, Y. Zhang, X. Zhang, L.-J. Zhang, J.-Q. Wang, J.-S. Hu, Z. Wei, L.-J. Wan, *Journal of the American Chemical Society* 2016, 138, 3570-3578.
- [20] H. L. Jiang, B. Liu, Y. Q. Lan, K. Kuratani, T. Akita, H. Shioyama, F. Zong, Q. Xu, J Am Chem Soc 2011, 133, 11854-11857.
- [21] P. Yin, T. Yao, Y. Wu, L. Zheng, Y. Lin, W. Liu, H. Ju, J. Zhu, X. Hong, Z. Deng, G. Zhou, S. Wei, Y. Li, *Angew Chem Int Ed Engl* **2016**, *55*, 10800-10805.
- [22] P. Chen, T. Zhou, L. Xing, K. Xu, Y. Tong, H. Xie, L. Zhang, W. Yan, W. Chu, C. Wu, Y. Xie, Angewandte Chemie-International Edition 2017, 56, 610-614.
- [23] J. A. Varnell, E. C. Tse, C. E. Schulz, T. T. Fister, R. T. Haasch, J. Timoshenko, A. I. Frenkel, A. A. Gewirth, *Nat Commun* **2016**, *7*, 12582.
- [24] C. H. Choi, W. S. Choi, O. Kasian, A. K. Mechler, M. T. Sougrati, S. Bruller, K. Strickland, Q. Jia, S. Mukerjee, K. J. J. Mayrhofer, F. Jaouen, Angew Chem Int Ed Engl 2017, 56, 8809-8812.

# Entry for the Table of Contents

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The removal of the metallic particles through a sulfur-assisted sites purification strategy to identify the main sites for catalytic contribution. The single-atom electrocatalysis occurred at the single-atom metal sites plays dominate roles in the ORR and HER processes of MOF-derived catalysts, especially for the ORR selectivity.



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Discrimination of the key singleatom electrocatalysis in MOFderived bifunctional catalysts