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Journal:	<i>Journal of Materials Chemistry A</i>
Manuscript ID	TA-ART-09-2023-005293.R1
Article Type:	Paper
Date Submitted by the Author:	01-Dec-2023
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1 Correlating the structural transformation and properties of ZIF-67 during  
2 pyrolysis, towards electrocatalytic oxygen evolution

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18 **Keywords:** *in situ* pyrolysis, heterogeneous electrocatalysis, metal-organic framework, structure-  
19 property relationship

20

## 1 Abstract

2 There is an emerging interest in using pyrolyzed metal-organic frameworks (MOFs) for electrocatalytic  
3 applications. While the MOF precursor and the final pyrolyzed catalyst are usually investigated, the  
4 pyrolysis process itself is often treated as a ‘black box’, and the phase transition is poorly understood as a  
5 result. The process further depends on the specific experimental setup, in terms of *e.g.* heating ramp, carrier  
6 gas and heat- and mass transport, complicating the comparison of catalyst properties across literature. In  
7 this study, we use *in situ* X-ray absorption spectroscopy and total scattering to elucidate the thermal  
8 decomposition of ZIF-67 to a MOF-derived nanomaterial (MDN), which is composed of cobalt  
9 nanoparticles embedded in a carbonaceous matrix. Furthermore, we demonstrate that the phase transition  
10 can be halted at different stages, allowing the corroboration of the *in situ* analyses with properties of *ex situ*  
11 MDNs produced by pyrolyzing ZIF-67 in a tube furnace at various temperatures and durations.

12 The electrochemical properties of the *ex situ* MDNs were studied systematically towards the oxygen  
13 evolution reaction (OER), facilitating the correlation of catalyst properties and structural characteristics for  
14 the ZIF-67 based catalysts. Although ZIF-67 is generally acclaimed for its thermal stability up to approx.  
15 400 °C, this study demonstrates the emergence of disorder at lower temperatures (approx. 150 °C). This  
16 disorder manifests as distortions of the framework by contraction of nearest neighbor Co-N, and an initial  
17 formation of cobalt clusters. Although this disorder resulted in poorer electrocatalytic performance relative  
18 to pristine ZIF-67, extending the temperature and duration of the pyrolysis process produced MDNs with  
19 superior electrochemical properties relative to pristine ZIF-67. The best catalyst exhibits the lowest  
20 overpotential against the oxygen evolution reaction of 416 mV, which is an improvement of 200 mV  
21 compared to the pristine MOF catalyst. The more heavily pyrolyzed samples are composed of cobalt  
22 nanoparticles with a bimodal size distribution at 1.4 nm and 7.1 nm (pyrolyzed at 550 °C for 8 or 12 h) and  
23 1.7 nm and 9.4 nm (pyrolyzed at 650 °C) confined in a carbonaceous matrix and with BET surface areas of  
24 40-130 m<sup>2</sup>g<sup>-1</sup>.

25

## 1        **1. Introduction**

2        Metal-organic frameworks (MOFs) composed of inorganic metal nodes and organic linkers have gained  
3        increased attention as electrocatalysts in recent years. MOFs not only offer a high degree of tuneability, but  
4        also high porosities and surface areas, which can expose a large number of active metal sites, resulting in a  
5        large mass activity per metal atom.<sup>1,2</sup> Despite these promising properties, MOFs are often plagued by low  
6        thermal and chemical stability, which results in restructuring or degradation of the frameworks under  
7        catalytic operating conditions.<sup>3-5</sup> One strategy which can overcome the low stability is to pyrolyze the MOFs  
8        in order to produce MOF-derived nanomaterials (MDNs). The resulting MDNs typically comprise metal  
9        and/or metal-oxide nanoparticles embedded in a carbonaceous matrix with a graphitic nature.<sup>6-10</sup> The  
10       graphitic carbon matrix can improve conductivity and hinder agglomeration of the nanoparticles formed  
11       during pyrolysis.<sup>11-14</sup> In addition, several properties of the parent MOF structure will be inherited by the  
12       MDN, such as porosity and morphology. The promising properties of the MDNs are therefore numerous,  
13       and these materials have proven to be highly effective and stable electrocatalysts.<sup>15-19</sup>

14       Mechanistic insights into the formation of MDNs are crucial for rational design of high-performance  
15       catalysts, however the pathway from MOF to MDN is generally poorly understood. Intermediate phases  
16       are often overlooked, as many studies only investigate the pristine and final compounds, and changes in the  
17       degree of order/disorder during the pyrolysis process are seldom studied. However, both the intermediate  
18       phases and degree of disorder are important to acknowledge, as they influence the properties of the final  
19       material. A small number of studies have elucidated the transient phase behavior and time/temperature  
20       dependence of the thermal treatment of MOFs by means of *in situ* X-ray diffraction (XRD), total scattering  
21       and pair distribution function (TS/PDF) analysis, and/or X-ray absorption spectroscopy (XAS).<sup>13, 20, 21</sup> The  
22       combination of these techniques details the transformation from MOF to MDN on both a local and long-  
23       range scale, thus mapping both crystalline and non-crystalline changes. When combined with catalytic  
24       studies, such detailed structural investigations enable correlations of the structural evolution with the  
25       catalytic properties throughout the different stages of the pyrolysis process. This strategy is in stark contrast

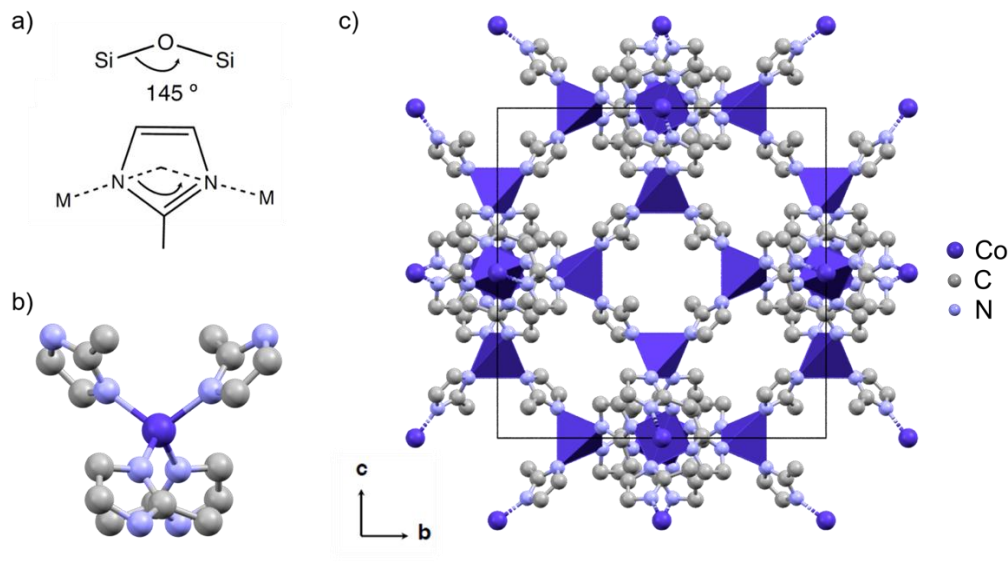
1 to studies that only focus on the pristine MOF and the end-product of pyrolysis as obtained in the lab. The  
2 structure and performance of the end-product will strongly depend on the specific pyrolysis conditions and  
3 makes comparison across literature challenging.

4 Zeolitic imidazole framework no. 67 (ZIF-67) is a widely studied cobalt-based MOF with a  
5 2-methylimidazolate (mIM) linker<sup>22</sup> (Fig. 1). Excellent electrocatalytic properties have been demonstrated  
6 for ZIF-67, both in its pristine and modified form. Pyrolyzed ZIF-67 has been shown to be active for various  
7 electrocatalytic reactions such as the oxygen reduction reaction (ORR),<sup>23-26</sup> the electrochemical N<sub>2</sub>  
8 reduction (ENR),<sup>27</sup> as well as water splitting, including both the hydrogen evolution reaction (HER) and  
9 the oxygen evolution reaction (OER).<sup>28</sup> The structure of pyrolyzed ZIF-67 is highly dependent on the exact  
10 pyrolysis conditions, and the relationship between the pyrolysis conditions and structure of the pyrolyzed  
11 product is not understood in detail. However, most studies agree that the product of the pyrolysis process  
12 consists of cobalt nanoparticles embedded in a nitrogen-doped carbon matrix.<sup>29, 30</sup> Pyrolysis is often  
13 performed at high temperatures, *i.e.* 700 °C and above.<sup>31-33</sup> However, the pyrolysis of ZIF-67 at elevated  
14 temperatures has been associated with aggregation of the formed metal nanoparticles<sup>34</sup> and a low catalyst  
15 yield due to a high mass loss.<sup>31</sup> Recent investigations have therefore pivoted towards the use of lower  
16 pyrolysis temperatures and extended pyrolysis durations.<sup>35-37</sup> Specifically, Wang *et al.* studied the  
17 microstructural features of cobalt precipitation, nitrogen loss, and the porous carbon matrix formation with  
18 *in situ* transmission electron microscopy (TEM) during pyrolysis of ZIF-67, over the temperature range of  
19 300 °C to 900 °C. They observed a tradeoff between the microstructural features and the ORR  
20 performance.<sup>29</sup>

21 In this work, we investigate the conversion of ZIF-67 to MDNs via pyrolysis. ZIF-67 derived catalysts have  
22 been prepared by pyrolysis at various conditions across literature to improve their OER performance.<sup>38-41</sup>  
23 However, a fundamental understanding of the effect of the pyrolysis conditions on the structure and  
24 catalytic activity for electrocatalytic OER is generally lacking. We hypothesize that the catalyst structure  
25 and properties are strongly dependent on the pyrolysis conditions. Further, we speculate on whether

1 pyrolysis held for longer durations will generally produce higher performing catalysts, or whether the  
2 presence of structural intermediates or disorder could contribute to improving catalytic properties. We  
3 address these questions by following the transition from ZIF-67 to MDN from room temperature to 550 °C  
4 by *in situ* X-ray absorption spectroscopy (XAS) and total scattering (TS) followed by pair distribution  
5 function (PDF) analysis. In addition, we explore the structure and electrochemical properties of a series of  
6 samples resulting from *ex situ* low-temperature pyrolysis at 550 °C for a variety of time durations, to mimic  
7 the conditions of the *in situ* studies. The structure and electrochemical properties for a MDN pyrolyzed at  
8 650 °C is also considered.

9 Our findings demonstrate that the best performing catalysts are prepared by pyrolysis at 550 °C for 8 or 12  
10 hours or by heating to 650 °C followed by cooling to room temperature (i.e. without holding the target  
11 temperature). The structure of the resulting catalysts can be described as cobalt nanoparticles with bimodal  
12 size distributions of 1-2 nm and 7-9 nm, respectively, which are embedded in a nitrogen-doped porous  
13 carbon matrix, which assists in preventing agglomeration of the nanoparticles. We propose that improved  
14 catalytic performance results from a trade-off among the size of the cobalt particles, the degree of  
15 graphitization of the carbon matrix, and the electrochemical active surface area (ECSA). Catalysts prepared  
16 at 550 °C without any isotherm maintain the long-range order of the original ZIF-67, and we observe that  
17 thermally induced disorder decreases the catalytic activity and stability. Importantly, the structures of the  
18 samples prepared *ex situ* are representative of the different stages of the ZIF-67-to-MDN transition as  
19 followed *in situ*, proceeding from pristine to disordered ZIF-67 followed by a gradual transition from ZIF-  
20 67 to metallic cobalt in a carbonaceous matrix. This study therefore demonstrates the feasibility of utilizing  
21 *in situ* methods to screen for suitable phase and order/disorder compositions, which modify catalytic  
22 properties.



1  
2 **Fig.1:** a) ZIFs are characterized by a zeolite-like angle of the metal-linker-metal connection of  $145^\circ$ , here  
3 with 2-methylimidazolate (mIM) as the linker. b) The tetrahedral coordination of cobalt with linkers in ZIF-  
4 67. c) The cubic crystal structure of ZIF-67 viewed in the *b,c*-plane (CCDC 671074<sup>22</sup>). The unit cell is  
5 shown in black, cobalt is shown in dark purple, nitrogen in light blue, and carbon in grey. Hydrogen atoms  
6 are omitted for the sake of clarity. The crystal structure is visualized using Mercury.<sup>42</sup>

7  
8 **2. Results and Discussion**

9 ZIF-67 was synthesized by a room temperature precipitation reaction in methanol<sup>43</sup> and phase-purity was  
10 verified through Rietveld refinement of PXRD data (Fig. S1). Thermogravimetric analysis (TGA) was  
11 performed to mimic the pyrolysis process, by heating from room temperature to a target temperature of 550  
12 °C with a heating ramp of  $3\text{ }^\circ\text{C min}^{-1}$ , resulting in 3 hours of heating. The experiment reveals an onset of  
13 decomposition at 400 °C and a mass loss of approx. 33% at 550 °C. When performing TGA with a faster  
14 heating ramp of  $25\text{ }^\circ\text{C min}^{-1}$ , a mass loss of only 2% was found during the 22 min of heating (Fig. S2),  
15 emphasizing the importance of the heating rate on the loss of organic material. However, the same mass

1 loss of 33% was achieved after holding the temperature at 550 °C for an additional 5 minutes, regardless of  
2 the heating ramp applied (Fig. S19).

### 3 **2.1 Following the phase evolution and disorder by *in situ* pyrolysis**

4 The MOF-to-MDN structural transformation was followed *in situ* by XAS and TS/PDF analysis, with a  
5 focus on the phase evolution and order/disorder transformation. These techniques are highly relevant for  
6 the study of crystallographically challenged structures (*e.g.* amorphous, nanosized, or defect-rich). XAS is  
7 an element-specific technique which provides information about the local structure around the absorbing  
8 atom and its oxidation state, whereas PDF gives complementary information about all the interatomic  
9 correlations in a material, extending over both the local and medium range order.

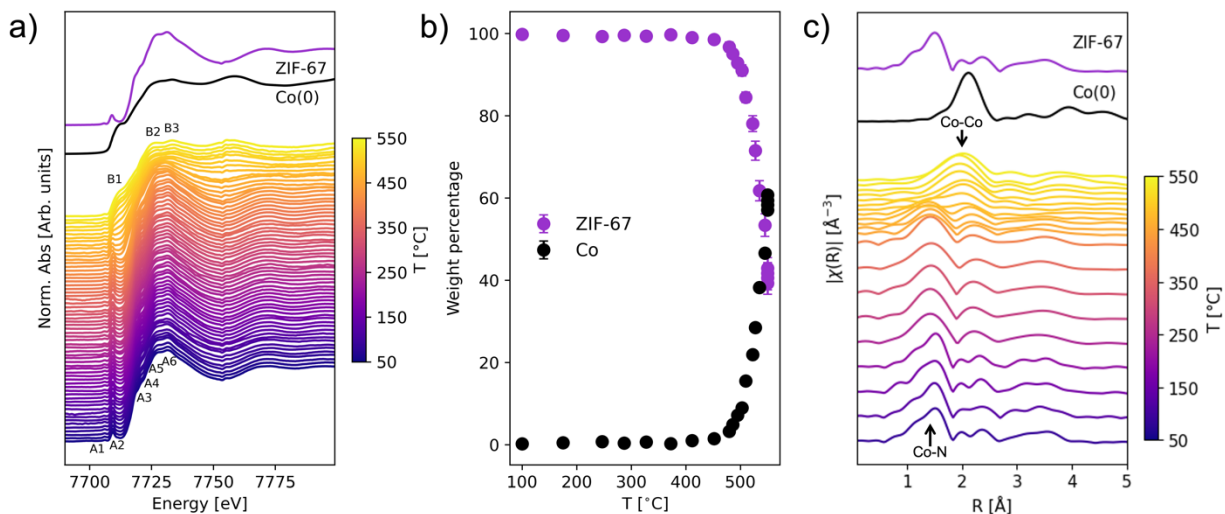
10 XAS and TS/PDF were used to follow the pyrolysis up to 550 °C with two different heating ramps: XAS  
11 with a slower ramp (3 °C min<sup>-1</sup>) and total scattering with a faster ramp (25 °C min<sup>-1</sup>). Two different setups  
12 were used for heating of the samples at the two beamlines (see Experimental section for details). However,  
13 the structural evolution during the phase transition is expected to follow the same mechanism.

#### 14 **2.1.1 *In situ* X-ray absorption spectroscopy**

15 The evolution of the oxidation state and local geometry of the cobalt atoms in ZIF-67 was investigated from  
16 the X-ray absorption near edge structure (XANES) region of the *in situ* XAS data, collected upon heating  
17 from room temperature to 550 °C at 3 °C min<sup>-1</sup> under a flow of inert gas. The data has been compared with  
18 that of the pristine ZIF-67 and metallic cobalt (Fig. 2a). The XANES region showcases the high thermal  
19 stability of ZIF-67, as the first changes to the spectral features occur after 3 h, at a temperature of approx.  
20 450 °C. Before this point, minimal changes to oxidation state or cobalt geometry are observed, *i.e.* cobalt  
21 is expected to be in the oxidation state of +II, and tetrahedrally coordinated to nitrogen atoms of the  
22 imidazolate linkers. The ZIF-67 XANES spectrum has characteristic features denoted A1-A6 in Fig. 2a.  
23 Above 450 °C, features corresponding to metallic cobalt gradually emerge. The sharp pre-edge feature (A2)  
24 of as-synthesized ZIF-67 at 7709 eV is broadened and shifted to a higher energy of 7712 eV (B1). The



1 features on the edge (A3 and A4) disappear, and the above edge features decrease in amplitude from approx.  
 2 1.2 to almost 1.0 in normalized absorption units, and split further in energies to 7726 eV (B2) and 7733 eV  
 3 (B3). The EXAFS oscillatory maximum at 7759 eV is also in agreement with metallic cobalt (Fig. 2a).  
 4 Thus, a qualitative fingerprint analysis demonstrates that ZIF-67 transforms gradually to metallic Co(0)  
 5 above 450 °C under inert conditions.



6  
 7 **Fig. 2:** a) *In situ* XANES spectra of ZIF-67 during pyrolysis at 3 °C min<sup>-1</sup>. The spectra are compared with  
 8 that of an as-synthesized sample of ZIF-67 and a metallic Co(0) foil as reference spectra. Features in the  
 9 ZIF-67 spectrum are annotated as A1-A6 and features of Co(0) as B1-B3. b) Phase content evolution during  
 10 ZIF-67 pyrolysis in weight percentage, based on LCA fitting. Two reference spectra were fitted to the data:  
 11 ZIF-67 and metallic cobalt. c) The Fourier transform magnitudes in *R*-space (not phase corrected) of the *in*  
 12 *situ* EXAFS compared to the spectra of pristine ZIF-67 and metallic cobalt. From room temperature to 450  
 13 °C, every ten spectra have been merged, while above 450 °C every two spectra have been merged to capture  
 14 the rapid changes.

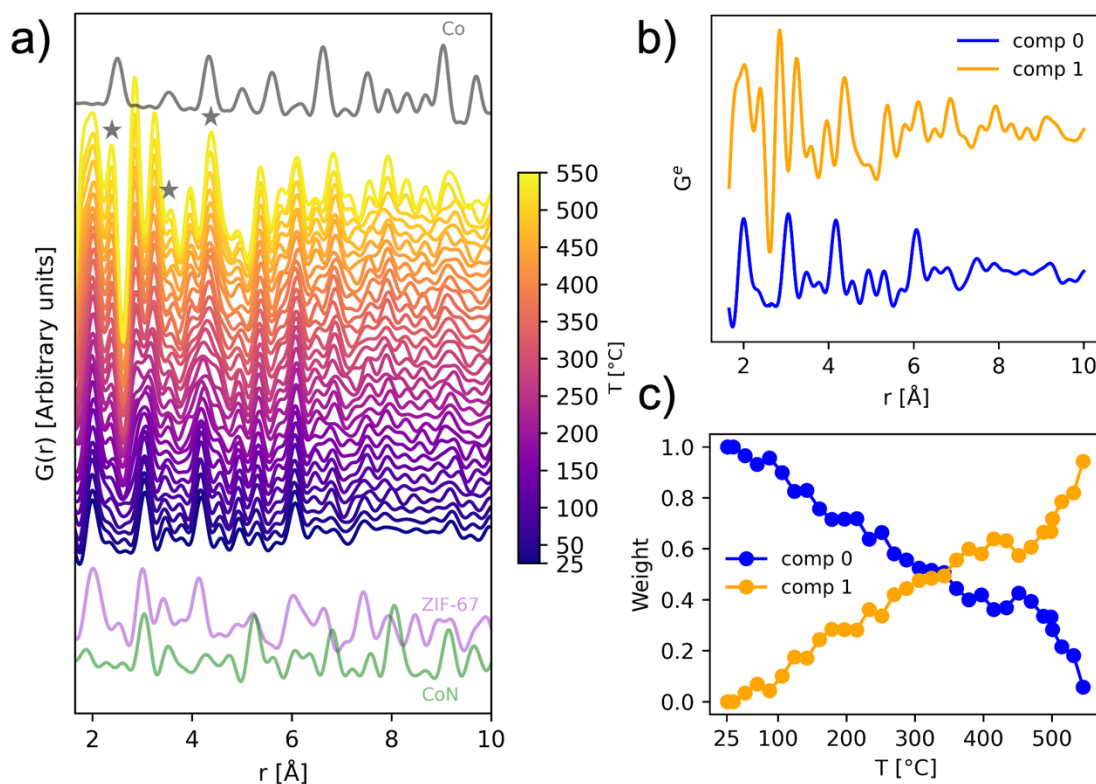
15 The structural transformation was quantified with linear combination analysis (LCA) with respect to  
 16 pristine ZIF-67 and metallic Co (Fig. 2b and S3, Table S2). A gradual change from ZIF-67 to Co is evident  
 17 above 450 °C. In a span of 100 °C, *i.e.* slightly more than 33 min (from 450 to 550 °C), the content of

1 ZIF-67 decreased from 98 wt% to 42 wt%. By instead performing LCA fitting against the first and last  
2 frame of the data series, the evolution with time is emphasized and indicates that the structural  
3 transformation is already initiated below 400 °C (Fig. S4-S5). In addition, there is no strong indication of  
4 intermediary cobalt oxide or nitride phases (Fig. S6).

5 Fourier transforms of the EXAFS region provide complementary information about the local structure  
6 around cobalt in real space (Fig. 2c, *k*-space EXAFS in Fig. S7). For pristine ZIF-67, the nearest neighbor  
7 Co-N gives rise to a peak at 1.5 Å, while the next-nearest neighbor Co-C is observed at 2.0 Å. Around 200  
8 °C a loss of features is observed, and the nearest neighbor peak broadens and downshifts to a slightly smaller  
9 distance of 1.4 Å (Fig. S8). This indicates that structural changes to the framework begin long before the  
10 reduction of the Co(II) species to Co(0), and given that no mass losses were observed from TGA (see Fig.  
11 S2) the increased disorder must stem exclusively from structural rearrangement. A gradual decrease in the  
12 intensity of the Co-N peak is observed at approx. 450 °C, while a simultaneous increase in intensity at 2.2  
13 Å corroborates the formation of Co-Co interactions (forming metallic cobalt), in agreement with the  
14 XANES analysis.

### 15 **2.1.2 *In situ* total scattering and pair distribution function (PDF) analysis**

16 In contrast to element-specific XAS, PDF additionally provides information on the structural correlations  
17 in the carbonaceous scaffold and allows for direct monitoring of the low-temperature structural changes as  
18 observed with EXAFS. Total scattering data were collected with a heating ramp of 25 °C min<sup>-1</sup> under a  
19 flow of inert gas (Fig. 3a).



1  
 2 **Fig. 3:** a) *In situ* PDF data during pyrolysis of ZIF-67, compared with the calculated PDFs of metallic cobalt  
 3 in grey (ICSD 76632<sup>44</sup>), ZIF-67 in purple (CCDC 671074<sup>22</sup>), and cobalt nitride in green (ICSD 79936<sup>45</sup>),  
 4 calculated with PDFgui.<sup>46</sup> The emergence of Co-Co peaks is highlighted with grey stars. b) NMF  
 5 components, and c) evolution of the two NMF components with temperature, given as the weight used to  
 6 recreate the experimental PDFs during the *in situ* series.

7 During the total scattering experiment, full decomposition of ZIF-67 is not observed (Fig. 3a and S9) due  
 8 to the fast heating ramp, which is in agreement with the TGA measurements (Fig. S2). Instead, gradual  
 9 changes are observed, with the system becoming increasingly disordered already at 100-300 °C, *i.e.* far  
 10 below the decomposition temperature, corroborated by the EXAFS results. For example, new peaks  
 11 describing Co-Co interactions start to emerge at approx. 150 °C (Fig. 3a).

12 The thermally induced structural disorder and phase transformation is further verified through non-negative  
 13 matrix factorization (NMF) analysis (Fig. 3b,c). Two components are sufficient to describe the structural

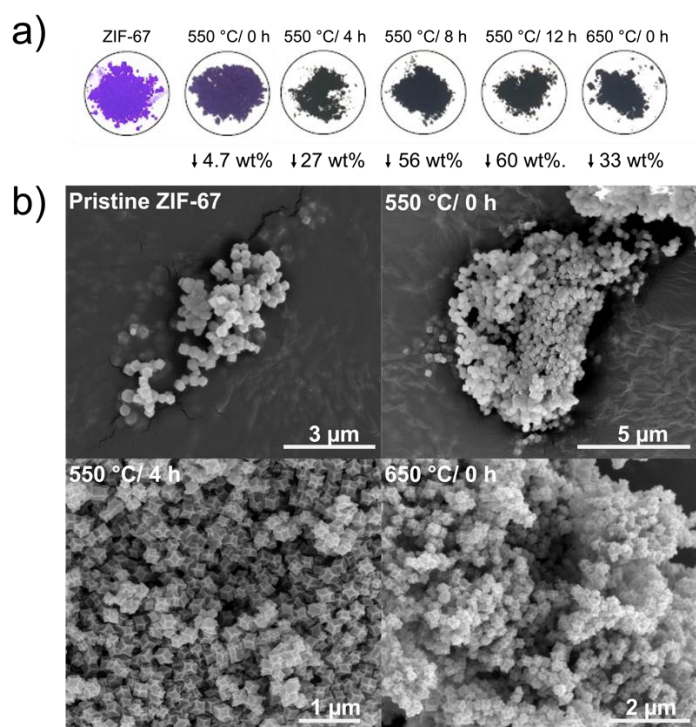
1 transformations (Fig. S10-S11), where local changes are predominant. The two components correspond to  
2 the first frame (component 0) and final frame (component 1) during the pyrolysis data series, *i.e.* at room  
3 temperature and at 550 °C. The evolution is followed through the relative abundance of component 0 and  
4 1, as required to approximate each dataset in the *in situ* series, referred to as weight (Fig. 3c). A linear  
5 change in the sample composition is observed until approx. 400 °C, where the composition stabilizes. This  
6 plateau is followed by an increase in the slope after 450 °C. Component 1 shows the emergence of Co-Co  
7 peaks below 6 Å as well as an additional peak from Co-N interactions at a lower distance of 1.9 Å (Fig.  
8 S12-S17 for assignment of peaks). Although bond lengths typically increase with temperature, both EXAFS  
9 and PDF analyses suggest contraction in the nearest metal to linker bond. This phenomenon has been  
10 reported previously during the pyrolysis process of other MOFs, possibly relating to changes in the ligand  
11 chemistry or distortions to the framework.<sup>20</sup> An intensity increase in the local Co-C peaks is also observed.  
12 As the ZIF-67 structure itself has numerous correlations, a complete peak assignment is not included herein.

13 In summary, the *in situ* XAS and PDF experiments provide several insights into the pyrolysis process. There  
14 is a good agreement between the two techniques, which suggest the formation of metallic cobalt progresses  
15 rapidly above 450 °C. No indications of crystalline or amorphous intermediates were observed according  
16 to LCA and NMF analyses. Overall, the *in situ* pyrolysis analyses disclose that transformations of the  
17 atomic structure take place even at several hundreds of degrees below the decomposition point, due to the  
18 indications of altered local Co-N, Co-C and Co-Co correlations, despite preservation of long-range order.  
19 Such information, which cannot be captured by *e.g.* conventional TGA or PXRD analysis, is important to  
20 acknowledge, given that temperature induced structural disorder may lead to differences in the materials  
21 properties.

22

## 2.2 *Ex situ* low-temperature pyrolysis for catalyst preparation

From the *in situ* investigations, structural transformations are evident below 550 °C, with induced disorder already observed at around 150 °C. Here, we explore the structural and catalytic properties of samples prepared by heating of pristine ZIF-67 under inert conditions, using a tube furnace with a heating ramp of 3 °C min<sup>-1</sup>, followed by an isothermal stage of different time durations. These samples are denoted *ex situ* samples herein and are intended to mimic the conditions used in the *in situ* study presented above, while allowing preparation of larger sample quantities *e.g.* for catalytic screening. Thus, five pyrolyzed ZIF-67 samples were produced by low-temperature pyrolysis (*i.e.* below 700 °C): four at 550 °C holding the target temperature for 0, 4, 8, and 12 h, and one at 650 °C with no subsequent isothermal step (Fig. 4a).



10

11 **Fig. 4:** a) Pictures of pristine and pyrolyzed ZIF-67 powders along with their associated mass loss. b) SEM  
12 images of pristine ZIF-67 (top left), and pyrolyzed ZIF-67 at 550 °C/ 0 h (top right), 550 °C/ 4 h (bottom  
13 left), and 650 °C/ 0 h (bottom right).

1 For the sample heated to 550 °C without any isothermal step (denoted 550 °C/ 0 h herein), the purple color  
2 of the pristine ZIF-67 is mostly preserved, however the final color is less bright than the pristine sample.  
3 Under these heating conditions, only a small mass loss of 4.7 wt% was observed (Fig. 4a). From the  
4 chemical formula of ZIF-67, it can be estimated that the imidazolate linker comprises 73.3 wt% of the  
5 material and cobalt the remaining 26.7 wt%. Thus, by heating to 550 °C/ 0 h, a large fraction of the organic  
6 components is preserved (in agreement with FT-IR analysis, Fig. S21). The observed mass loss is similar  
7 to the expected value from TGA, although slightly lower, which is attributed to the differences in the sample  
8 mass load and in the efficiency of heat transport between the tube furnace and the TGA (Fig. S22). After  
9 isothermal heating for 8 and 12 hours, respectively, a black powder results, and the mass loss stabilizes at  
10 approx. 60 wt%, as corroborated by the isothermal segment of the TGA (Fig. S18-S22).

11 Both pristine and pyrolyzed ZIF-67 exhibit a uniform polyhedral morphology and size distribution, with  
12 particle sizes of 200 nm estimated from scanning electron microscopy (SEM) and transmission electron  
13 microscopy (TEM) images (Fig. 4b and S23-S24). After pyrolyzing the MOF for 4 hours at 550 °C, the  
14 crystals appear somewhat collapsed, with defined edges and indented facets, which is also observed for the  
15 sample pyrolyzed at 650 °C/ 0 h. Scanning transmission electron microscopy (STEM) combined with  
16 energy dispersive X-ray spectroscopy (EDS) confirm that the product of the pyrolysis process comprises  
17 cobalt nanoparticles encapsulated in a nitrogen-doped graphitic network, which is a product of the  
18 decomposition of the organic components (Fig. S25-26), in agreement with literature.<sup>26,29,30,47</sup>

19 The compound surface areas were investigated through nitrogen adsorption-desorption isotherms (Fig.  
20 S27). The Brunauer-Emmett-Teller (BET) specific surface areas based on the gas sorption data (Table S5)  
21 show a loss of porosity as a result of the pyrolysis process, when comparing the pristine ZIF-67 (1272 m<sup>2</sup>g<sup>-1</sup>)  
22 to the 550 °C/ 0 h sample (905 m<sup>2</sup>g<sup>-1</sup>). With the exception of the 550 °C/ 12 h sample, all samples  
23 pyrolyzed at higher temperatures or durations have a surface area below 100 m<sup>2</sup>g<sup>-1</sup>.

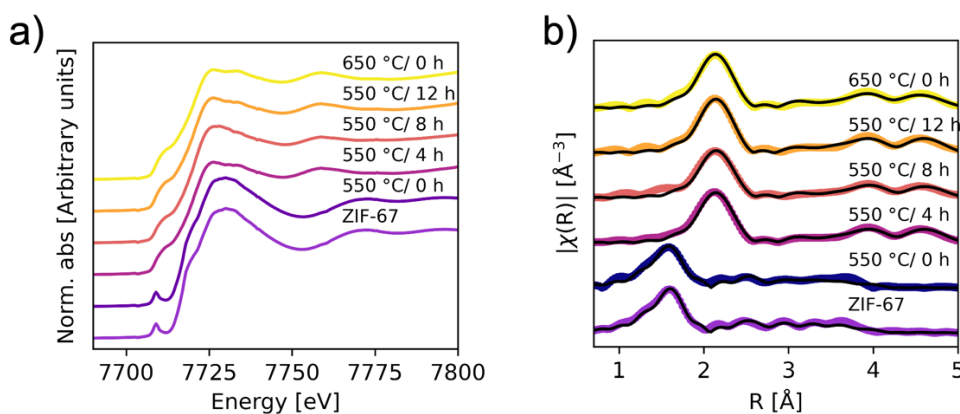
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1

2

### 2.2.1 Structural characterization by X-ray scattering and absorption spectroscopy

3 XAS measurements performed on the *ex situ* samples (Fig. 5) indicate a high level of similarity between  
4 the 550 °C/ 0 h sample and the pristine ZIF-67, which is in stark contrast to the *in situ* experiment. This  
5 indicates that the *ex situ* heating process to 550 °C does not change the oxidation states nor the local  
6 coordination of the cobalt atoms in the MOF, despite using the same heating ramp as was used in the *in situ*  
7 experiments. We ascribe the negligible impacts of the short term pyrolysis process for the *ex situ* sample to  
8 a smaller global heat transfer coefficient in comparison with the *in situ* experiments (Fig. S22). This is  
9 mostly due to differences in the setups (acting on the thermal convection and radiation) as well as the  
10 amount of sample used (thermal conduction). After prolonged pyrolysis at 550 °C or heating at 650 °C with  
11 no isotherm, a complete description of the local cobalt structure can be achieved by fitting with solely Co-  
12 Co scattering paths (Fig. S28), indicating the presence of cobalt as cobalt nanoparticles (Fig. 5b). This  
13 fitting result does not exclude the presence of other phases, as Co-Co correlations dominate the EXAFS  
14 due to the scattering power of Co.



15

16 **Fig. 5:** XAS on the *ex situ* pyrolyzed samples. a) XANES data. b) Fourier transform of the EXAFS (not  
17 phase corrected). Spectra of the pristine and 550 °C/ 0 h samples are fitted by using scattering paths  
18 calculated from the ZIF-67 structure, while the remaining spectra are fitted with the paths from metallic Co  
19 (fcc). The scattering paths were calculated in Artemis.<sup>48</sup>

1 The phase content of the samples was obtained through LCA fitting (Fig. S29-S30 and Table S6). The 550  
2 °C/ 0 h sample is exclusively described by the pristine ZIF-67 phase, while prolonging the pyrolysis  
3 durations increase the amount of metallic cobalt. However, the cobalt content is significantly lower than  
4 that obtained from the *in situ* measurement at 550 °C. This difference suggests that the *in situ* heating  
5 process results in faster decomposition, as corroborated by the lower mass loss, which can be explained by  
6 differences in heat transport. The final weight fraction of metallic cobalt was 60% in the *in situ* XAS  
7 experiment, compared with 45% after 4 hours of pyrolysis at 550 °C and 56% at 650 °C/ 0 h. The 650 °C/  
8 0 h sample, is thus expected to be the best representation of the end-point of the *in situ* XAS pyrolysis,  
9 corroborated by the heat transport differences (Fig. S22). An improvement in the LCA fits was observed  
10 upon including the Co(II) oxide species (Fig. S30-S32 and Table S7). The ratio of ZIF-67 to cobalt(II)  
11 oxide varies marginally between samples prepared at 550 °C/ 4 h, 8 h, 12 h, and the 650 °C/ 0 h sample at  
12 approx. 15% cobalt(II) oxide. The presence of cobalt(II) oxide in the *ex situ* samples likely arises due to  
13 surface oxidation of the samples after pyrolysis, in contrast to the *in situ* samples which were kept in inert  
14 conditions throughout the entire experiment. The sample compositions for the 550 °C/ 4 h, 8 h, 12 h, and  
15 650 °C/ 0 h samples have similar values within 15% difference, which is also expected from TGA data.

16 The long-range order of the samples was investigated with PXRD (Fig. 6a), demonstrating that the structure  
17 is still preserved when the sample is heated to 550 °C/ 0 h, which corroborates the *ex situ* XAS results.  
18 Upon longer pyrolysis exposures, a phase transformation occurs, and broader peaks are observed along  
19 with a high background signal, attributed to the amorphous carbonaceous matrix. The broad peak at 37° fits  
20 well with the (002) reflection of graphite. Two distinct peaks of metallic Co are present, but very broad,  
21 signifying small crystallites. Pyrolysis for 8 and 12 hours at 550 °C results in additional diffraction peaks  
22 that can be described by the reflections of CoN and/or CoO, in agreement with the proposed presence of  
23 Co(II) oxide as derived from the LCA fitting. However, these are not visible as crystalline components for  
24 the 550 °C/ 4 h and 650 °C/ 0 h samples, which from the TGA alone would be expected to have similar

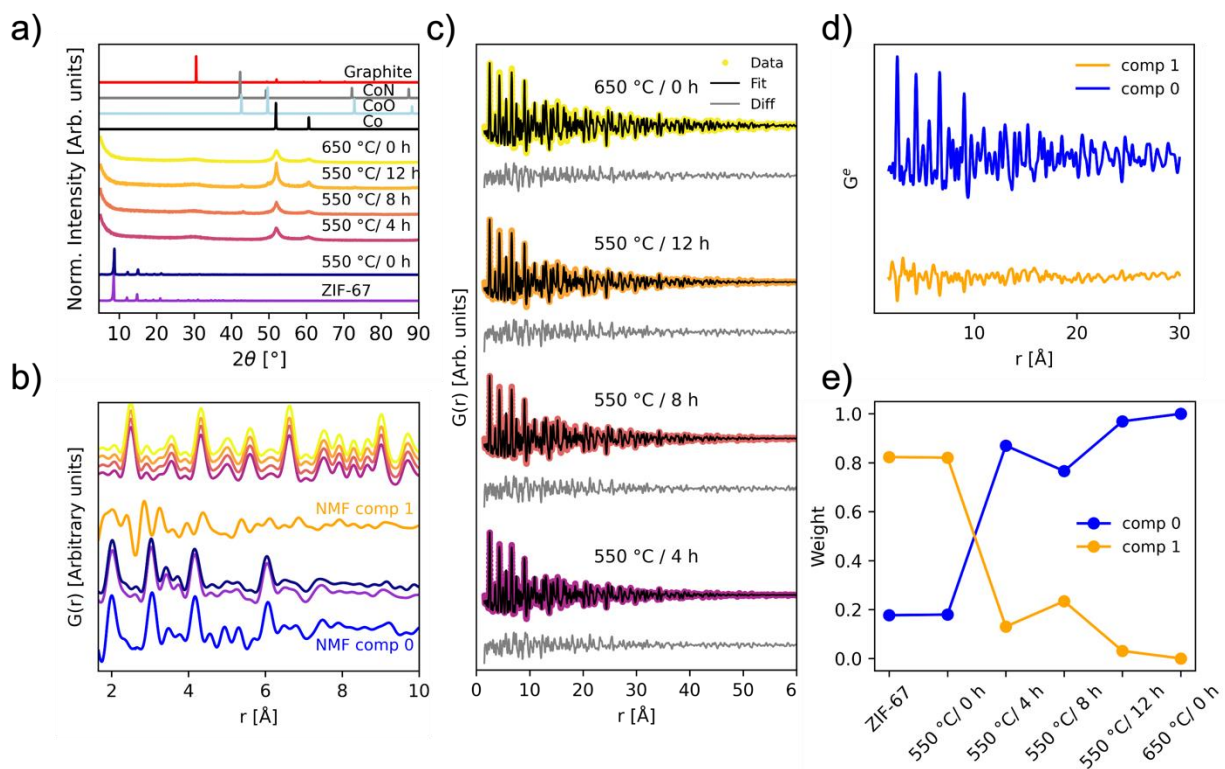


1 characteristics. To gain insight into the nanostructure of the materials, PDF analysis was employed using  
2 total scattering data.

3 PDFs of the pyrolyzed samples are shown in Fig. 6b-c. A transformation into metallic Co nanoparticles for  
4 the samples pyrolyzed at 550 °C for 4 hours or longer is observed in the PDFs, in agreement with EXAFS  
5 and PXRD analyses (Fig. 5b and 6a). Locally, the structure of the 550 °C/ 0 h sample is very similar to the  
6 pristine ZIF-67, although more disordered. Especially above 10 Å, features appear less pronounced, which  
7 points to a loss of long-range order during the short-term heating process (Fig. S33). The new correlations  
8 observed during the *in situ* pyrolysis are not detected in the *ex situ* 550 °C/ 0 h sample when comparing  
9 with NMF comp 1, which represents the final state structure of the *in situ* series. However, the emergence  
10 of the peaks at approx. 2.5 Å and 5 Å, as seen in NMF comp 1, fits well with the first Co-Co correlations  
11 observed in the sample pyrolyzed at 550 °C for 4 hours or longer (Fig. 6b). Thus, the *in situ* PDF results  
12 represent intermediary stages in the transition from the pristine ZIF-67, to a similar, but more disordered  
13 structure, and finally into metallic cobalt. We conclude that the *in situ* experiments are representative of the  
14 processes used in the production of in-lab scaled-up *ex situ* samples.

15 The structure of metallic cobalt has been fitted to the samples which were pyrolyzed for longer durations  
16 (Fig. S34, Table S8). To account for the envelope function not capturing the shape properly, two phase fits  
17 were performed with two Co-phases with different sizes (Fig. 6c, Table S9). This improved the residual at  
18 long distances, but locally, the data is still underdetermined. Variable *r*-range fits did not resolve the  
19 underdetermined peaks (Fig. S35-S38). This suggests that the local structure ( $r < 9$  Å) is disordered. The  
20 two particle sizes of the cobalt in the pyrolyzed samples were determined to be 1.4 nm and 6.5 nm for the  
21 550 °C/ 4 h sample, 1.4 nm and 7.0 nm for the 550 °C/ 8 h sample, 1.4 nm and 7.1 nm for the 550 °C/ 12 h  
22 sample, and 1.7 nm and 9.4 nm for the 650 °C/ 0 h sample. These results suggest that the cobalt particles  
23 reach a size of approx. 7 nm, and thereafter stop growing, despite longer pyrolysis times at 550 °C, which  
24 supports the hypothesis that the carbon matrix hinders agglomeration, and an equilibrium is reached. These  
25 particle sizes are similar to those observed with TEM herein (Fig. S23-24) and also to those previously

1 reported via TEM by others.<sup>29</sup> For the 650 °C/ 0 h sample, larger particles up to 9.4 nm are observed, which  
 2 could arise due to thermally induced changes in the carbon matrix, which then allow for the formation of  
 3 larger cobalt particles. These observations suggests that the *ex situ* pyrolysis conditions are not temperature-  
 4 independent, despite that the TGA results indicate a temperature independent mass loss and a low activation  
 5 energy (Fig. S20).



6  
 7 **Fig. 6:** *Ex situ* scattering experiments. a) PXRD patterns compared with calculated diffraction patterns of  
 8 graphite (ICSD 31170<sup>49</sup>), CoN (ICSD 79936<sup>45</sup>), CoO (ICSD 9865<sup>50</sup>), and Co metal (ICSD 76632<sup>44</sup>). b) PDF  
 9 of the local structure with identical color coding as in a), compared with NMF components from the *in situ*  
 10 experiment. c) Two-phase PDF refinements of the four pyrolyzed samples that have converted into metallic  
 11 Co. d) NMF components, and e) the weight of the NMF components used to recreate the experimental  
 12 PDFs of each of the *ex situ* samples.

13 NMF analysis of the *ex situ* samples confirms the structural similarity between the pristine ZIF-67 and the  
 14 sample pyrolyzed at 550 °C/ 0 h, as they share the same weight of NMF components (Fig. 6d,e). The 550

1 °C/ 8 h sample is slightly different from the other *ex situ* samples pyrolyzed for longer durations at 550 °C  
2 or at 550 °C, despite that the 8 and 12 hour samples have similar particle sizes. Thus, the differences are  
3 proposed to result from changes of the graphitic C/N matrix. Inclusion of a third component did not  
4 noticeably improve the reconstruction errors (Fig. S39), although a striking similarity in the weight of  
5 components is observed compared to the LCA with the CoO phase included (Fig. S30).

6 In summary, our findings demonstrate that absolute conditions are difficult to transfer between different  
7 setups, and further, that this is important both when using *in situ* studies to screen for transition  
8 temperatures, intermediates, etc. and also when comparing results from different setups for *ex situ* sample  
9 preparation in the lab. Despite this difficulty, it is possible to halt the pyrolysis process at different stages  
10 to screen and tune the material properties, for example “trapping” of a sample with increased disorder in  
11 the carbon matrix. While TGA captures the slow process of reaching equilibrium, this technique alone  
12 cannot be used as a proxy for the catalyst composition. There is a good agreement between the three  
13 techniques, *i.e.* XAS, PXRD, and PDF, and the mechanism of the phase transition observed *in situ* can  
14 describe the pyrolysis of ZIF-67 *ex situ*. Overall, we find that pyrolysis of ZIF-67 to 550 °C without an  
15 additional isothermal heating step (*i.e.* 550 °C/ 0 h) induced thermal disorder, whilst preserving the long  
16 range order of ZIF-67. After pyrolysis at 550 °C for 4 hours or longer, cobalt nanoparticles are formed.  
17 Two particle sizes were found to describe the particles distribution, one of them representing small cobalt  
18 clusters of approx. 1-2 nm (corresponding to 7 atoms across the diameter). After pyrolysis at 550 °C for 8  
19 or 12 hours, the cobalt nanoparticles reach a maximum size of 7 nm, and are stabilized within the C/N  
20 matrix.

21

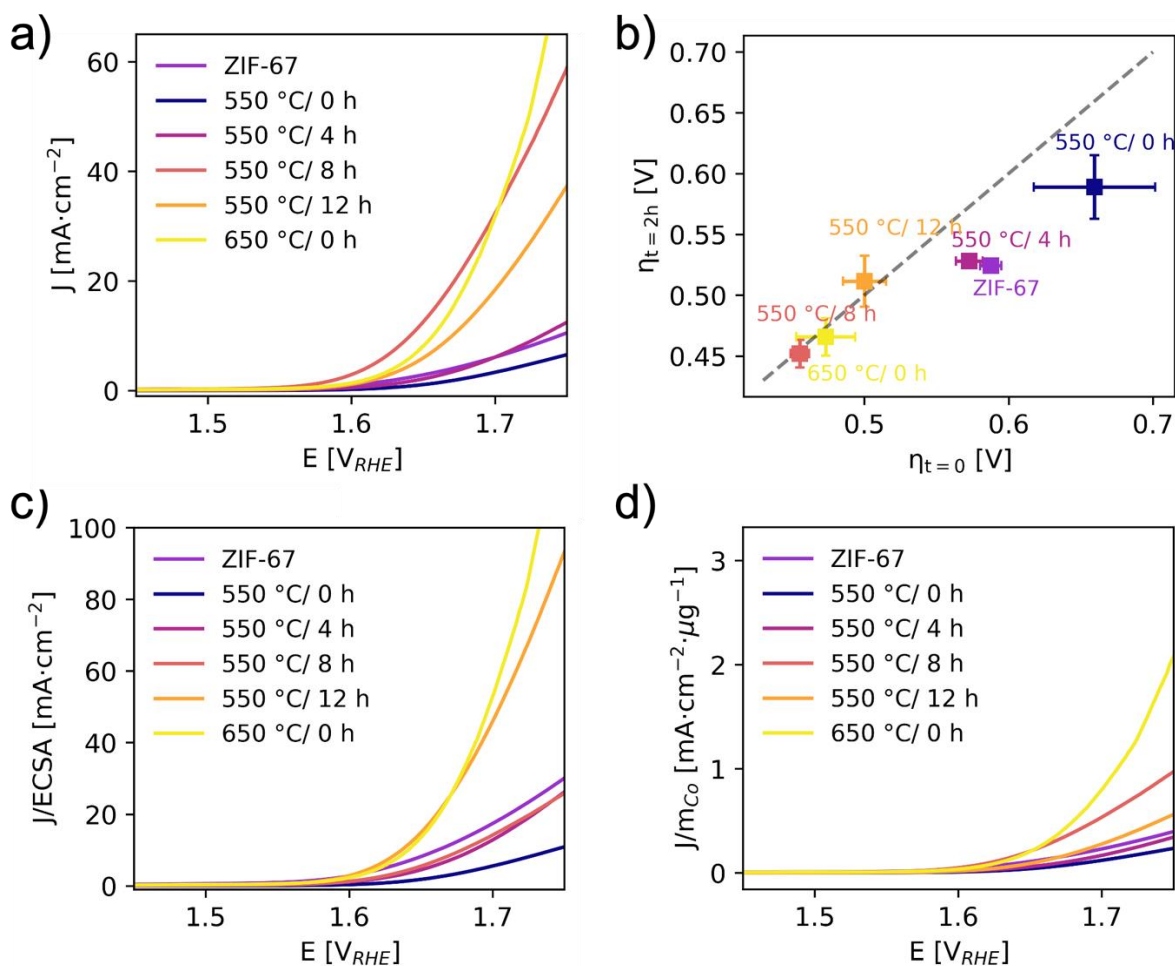
### 22 **2.3 Electrocatalytic Oxygen Evolution Reaction**

23 In this section, the electrocatalytic oxygen evolution reaction (OER) activity of the *ex situ* samples is  
24 explored. We evaluate the influence of pyrolysis on activity and stability, and attempt to correlate this to

1 the following descriptors: atomic structure, particle size, electrochemical active surface area (ECSA), and  
2 the relative cobalt content.

3 Equal amounts of the pyrolyzed samples (by mass) were deposited on carbon paper electrodes with a Nafion  
4 binder. Linear sweep voltammetry (LSV) was performed in 1 M KOH<sub>(aq)</sub> electrolyte with a scan rate of  
5 10 mV s<sup>-1</sup> (Fig. 7). Five sweeps were performed (sweep 1-4 in Fig. S40, sweep 5 Fig. 7a), and an activation  
6 of all materials was detected. The electrochemical activity falls within two groups. The activity of the  
7 catalysts in the first group is either lower or comparable with that of the pristine ZIF-67, including the 550  
8 °C/ 0 h and 550 °C/ 4 h samples. The catalysts in the second group exhibit activity which is significantly  
9 higher than that of the pristine ZIF-67, with this group accounting for the catalysts pyrolyzed for longer  
10 duration or higher temperature, *i.e.* 550 °C/ 8 h, 550 °C/ 12 h, and 650 °C/ 0 h.

11



1  
 2 **Fig. 7:** a) Linear sweep voltammetry with a scan rate of 10 mV s<sup>-1</sup>. b) Overpotentials were determined from  
 3 chronopotentiometry at  $J=10$  mA cm<sup>-2</sup> per geometric area. The  $x$ -axis represents the overpotential at time  
 4  $t = 0$ , as a measure of activity. The  $y$ -axis represents the overpotential at time  $t = 2$  h. The diagonal dashed  
 5 line is the expected response for a stable catalyst, and deviations from this indicate an unstable catalyst.<sup>51</sup>  
 6 c) LSV responses normalized to the ECSA (from capacitance measurement, see Fig. S43). d) LSV  
 7 responses normalized to the mass of cobalt calculated considering the final Co wt% after pyrolysis under  
 8 the assumption that the mass loss during pyrolysis is entirely associated to the (volatile) organic linker (Fig.  
 9 S48).  
 10 In Fig. 7b, the overpotentials are estimated as the electrical bias needed at the anode to draw a current  
 11 density of  $J=10$  mA cm<sup>-2</sup>, and their reliability was checked against other standard methods (Fig. S47). The

1 worst electrochemical performance is observed for the catalyst pyrolyzed at 550 °C/ 0 h with an  
2 overpotential of  $\eta_{\text{current}} = 619$  (47) mV. The decrease in electrochemical activity of this catalyst compared  
3 to the structurally similar pristine ZIF-67 is attributed to the more disordered local structure (from PDF,  
4 Fig. S33) and also the lesser microporosity (from BET, Fig. S27).

5 The activity was significantly improved for catalysts prepared at 550 °C and held at this temperature for 8  
6 and 12 hours, as well as the catalyst pyrolyzed at 650 °C/ 0 h. For both 550 °C/ 8 h and 550 °C/ 12 h, the  
7 mass loss was stable (based on TGA, Fig. S22 and Fig. 4a) and a stable particle size of approx. 7 nm was  
8 reached (based on PDF refinements, Fig. 6c). The main structural differences for catalyst pyrolyzed at 650  
9 °C/ 0 h are the larger cobalt nanoparticle size and the higher fraction of organic components remaining  
10 (according to the mass loss, Fig. 4a). The 550 °C/ 8 h catalyst achieves the lowest overpotential of  $\eta_{\text{current}}$   
11 = 416 (3) mV (Fig. S42). A smaller particle size is generally considered to be beneficial for catalytic  
12 applications, but despite that the 550 °C/ 4 h catalyst contains the smallest cobalt nanoparticles, this catalyst  
13 performs worse (with  $\eta_{\text{current}} = 516$  (12) mV) than the remaining catalysts which were pyrolyzed for longer  
14 durations. This is hypothesized to be due to a different nature of the organic components. A higher graphitic  
15 degree of the organics-derived matrix will improve the electrical conductivity and electron transport  
16 through the catalyst, and is observed in literature with increased pyrolysis temperature/time.<sup>29, 31</sup> From  
17 PXRD (Fig. 6a), the presence of a broad graphite peak is visible for all samples converted to metallic cobalt,  
18 however we expect the 550 °C/ 4 h catalyst to have a poorer graphitic degree compared to both the 650 °C/  
19 0 h catalyst and to the 550 °C/ 8 h and 550 °C/ 12 h catalysts.

20 The short-term stability under working conditions was then explored with chronopotentiometry at 10 mA  
21  $\text{cm}^{-2}$  for 2 h, which is the current density expected at the anode in a 10% efficient solar water-splitting  
22 device under 1 sun illumination.<sup>52-54</sup> Representative evolutions of the potential as a function of time for  
23 each catalyst are shown in Fig. S45. The overpotentials required in the beginning,  $\eta_{t=0}$ , and after 2 hours,  
24  $\eta_{t=2\text{ h}}$ , are reported (Fig. 7b). The pristine ZIF-67, 550 °C/ 0 h, and 550 °C/ 4 h catalysts all show a significant  
25 decrease in their overpotentials after 2 hours, which corresponds to an activation of the catalyst. The

1 catalysts pyrolyzed for longer durations and at 650 °C/ 0 h, on the other hand, appear stable under operating  
2 conditions. This supports our hypothesis that a higher degree of pyrolysis results in a more stable catalyst.  
3 The activity is normalized to the ECSA (Fig. 7c), with the ECSA determined from the double layer  
4 capacitance of the catalytic surface.<sup>55</sup> This was determined by measuring the capacitive current associated  
5 with the double-layer charging in a non-Faradic region through cyclic voltammetry at different scan rates  
6 (Fig. S43). The 550 °C/ 8 h catalyst stands out with the highest double layer capacitance of 0.09 mF  
7 compared to 0.01-0.02 mF for the rest. Thus, its high activity can be partially ascribed to surface area  
8 effects, *i.e.* more exposed active sites and a more nanostructured surface. The 550 °C/ 12 h and 650 °C/ 0  
9 h catalysts still exhibit the highest normalized activity. When the electrochemical performances of the  
10 catalysts are compared with the ECSA metric, it appears even more evident that the samples pyrolyzed at  
11 the longest time or at the highest temperature share similar improved performance with respect to the other  
12 catalysts. This is in accordance with their structural similarity as highlighted before. Strikingly, the trend in  
13 ECSA does not follow the surface area as determined from BET, which is indicative of the catalyst porosity  
14 (Fig. S27, Table S5). Here the 550 °C/ 4 h and 550°C/ 8 h catalysts stand out as the densest samples with  
15 areas of 40 and 42 m<sup>2</sup> g<sup>-1</sup>, which is only half the surface area of the 650 °C/ 0 h and a third the surface area  
16 of the 550 °C/ 12 h catalyst.

17 The activity was also normalized to the cobalt mass  $m_{\text{Co}}$  as determined from the mass loss during pyrolysis  
18 under the assumption that the mass loss only comprised the organic linker, while the absolute Co content  
19 remained constant (Fig. 7d). A large mass loss during pyrolysis results in a higher relative amount of cobalt  
20 in the catalysts. Similar activity and overpotential were determined for the 650 °C/ 0 h and the 550 °C/ 8 h  
21 catalysts. The 650 °C/ 0 h catalyst exhibits lower mass loss, and this catalyst exhibits the highest  
22 performance in terms of mass activity per cobalt. Thus, from an economic point of view, the 650 °C/ 0 h  
23 sample would be the optimal catalyst in this series.

24 In conclusion, tuning of pyrolysis conditions can greatly influence the electrocatalytic properties. Literature  
25 examples of ZIF-67-derived and -modified catalysts (*e.g.* nanostructuring<sup>38</sup>, multi-heteroatom co-doping,<sup>39</sup>

1 interface engineering and heterostructure formation,<sup>40</sup> and defect engineering<sup>41</sup>) have shown good OER  
2 performances (see Table S10 for a comparison of electrocatalytic performance of ZIF-67 based and cobalt  
3 based catalysts). As many of these modification procedures involve pyrolysis steps, a fundamental  
4 understanding of the impact of pyrolysis conditions alone, rather than combined pyrolysis and *e.g.* chemical  
5 modification, is of paramount importance to decouple contributors to catalytic performance.

6 Several structural characteristics have been explored for a series of *ex situ* samples, including phase  
7 composition, cobalt nanoparticle size, porosity, and ECSA. The question remains, if one of these parameters  
8 dominates in controlling the OER properties of pyrolyzed ZIF-67, and if this parameter can potentially be  
9 used as a structural indicator for predicting good electrochemical activity of similar materials. To  
10 summarize the findings from this structure-activity study: (i) Pyrolysis at long time/high temperature gives  
11 a more stable sample and better OER performance, (ii) Induced disorder in ZIF-67 arising due to short  
12 pyrolysis time does not result in defect sites acting as active sites, (iii) There is no direct trend between the  
13 BET surface area and the ECSA, (iv) The nanoparticle size is constant for the catalysts pyrolyzed at 550 °C  
14 for 8 and 12 hours, and this parameter therefore cannot explain the difference in activity between these two  
15 catalysts. Thereby, our findings demonstrate that electrochemical performance is a complex combination  
16 of a series of parameters: framework stability obtained through pyrolysis, small Co particles acting as active  
17 sites, possibly the degree of graphitization increasing with pyrolysis time/temperature, and exposure of the  
18 active sites as indicated by the ECSA. This complex catalyst structure heavily depends on the synthesis,  
19 and demonstrates the importance of detailed structural characterization in the description and comparison  
20 of pyrolyzed MDNs.

21

## 22 **Conclusion**

23 In this work, we investigated the structure-activity relationship of a series of pyrolyzed ZIF-67 OER  
24 catalysts. Unravelling the structural changes during pyrolysis through a combination of *in situ* XAS and



1 PDF together with *ex situ* structural probes reveals the decomposition of ZIF-67 into a MDN consisting of  
2 metallic cobalt nanoparticles within a nitrogen-doped graphitic carbon matrix. The onset of decomposition  
3 occurs at 450 °C, although structural changes and induced disorder are observed from 150 °C, where the  
4 nearest neighbor Co-N contracts as a result of framework distortions, and the first Co-Co peaks emerges  
5 below 6 Å.

6 We conclude that absolute conditions (*i.e.* pyrolysis temperature and time) are difficult to transfer between  
7 setups, both between the two *in situ* techniques as well as for the *ex situ* prepared catalysts. Thus, this study  
8 materializes the general challenge of comparing results between different setups across literature.  
9 Importantly, however, we find that the *in situ* mechanisms can describe the *ex situ* pyrolysis, and that the  
10 phase transition can be halted at different stages, *i.e.* as a disordered material with ZIF-67 long range order  
11 (550 °C/ 0 h) and as cobalt nanoparticles with different sizes stabilized by the nitrogen doped carbonaceous  
12 matrix (550 °C with 4, 8, 12 hours isotherms and 650 °C/ 0 h).

13 The catalytic efficiency of the samples was evaluated by their OER performance. These experiment series  
14 demonstrate that the best performing catalysts, both in terms of activity and stability, are pyrolyzed at the  
15 longest time and highest temperature. These catalysts are best described as cobalt nanoparticles with a  
16 bimodal size distribution, which are embedded in a highly graphitized carbonaceous matrix. The best  
17 performing catalysts exhibit a compromise between the size of the Co nanoparticles and the degree of  
18 graphitization. For comparison, thermally induced disorder in ZIF-67 lowers both the stability and activity  
19 in contrast to the pristine material.

20 Overall, the findings presented in this work pave the way for rational design of catalysts by utilizing  
21 pyrolysis at lower temperatures and combining *in situ* and *ex situ* structural techniques.

### 1        3. Experimental Section

2        All chemicals were purchased from Sigma-Aldrich and used without further purification.

#### 3        **Synthesis of ZIF-67**

4        Crystalline ZIF-67 was synthesized according to the reported procedure:<sup>43</sup>  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  (1.43 g 7.8  
5        mmol) and 2-methylimidazole (mIM, 3.24 g, 39.5 mmol) were each dissolved in 100 mL methanol. The  
6        two solutions were mixed and left to stir for 15 min, and subsequently left for 24 hours without stirring.  
7        The product was obtained by centrifugation, washed twice with methanol, and dried in an oven at 70 °C.  
8        The product was a fine purple powder.

#### 9        **Synthesis of *ex situ* pyrolyzed samples**

10       The as-synthesized ZIF-67 was pyrolyzed in a Nabertherm tube furnace with a heating ramp of 3 °C min<sup>-1</sup>  
11       with a 0.1 L min<sup>-1</sup> N<sub>2</sub> flow. Five samples were prepared: one at 550 °C with no further heating at the target  
12       temperature (550 °C/ 0 h), three at 550 °C with isothermal heating at the target temperature for several  
13       hours (4, 8, and 12 hours) to give the 550 °C/ 4 h, 550 °C/ 8 h and 550 °C/ 12 h samples, respectively, and  
14       one at 650 °C with no further heating (650 °C/ 0 h). The samples were left to cool naturally in the oven.

#### 15       **X-ray absorption spectroscopy**

16       *In situ* XAS was performed at the K edge of cobalt (7709 eV) in transmission mode at the B18 beamline at  
17       the Diamond Light Source in Oxford, UK.<sup>56</sup> A capillary furnace setup, provided by the beamline, was used.  
18       To obtain a suitable absorption edge step, powder of ZIF-67 was diluted with boron nitride and pressed to  
19       a pellet. The powder composition was estimated using the software XAFSmass.<sup>57</sup> A part of the pellet was  
20       inserted into a 3 mm quartz capillary, which was connected to the beamline mass flow controllers using  
21       Swagelok tubing, and the sample was purged by a nitrogen flow of 100 mL min<sup>-1</sup>. The sample was heated  
22       from room temperature to 550 °C by indirect resistance heating at a heating ramp of 3 °C min<sup>-1</sup>.  
23       Transmission spectra covering both the X-ray absorption near-edge structure (XANES) and the extended

1 X-ray absorption fine structure (EXAFS) region (200 eV below the edge to 850 eV above the edge) were  
2 collected in continuous scan mode with an acquisition time of approx. 90 seconds per spectrum. The X-ray  
3 energy was selected using a double crystal Si(111) monochromator, and spectra on a cobalt metal foil were  
4 measured simultaneously for energy calibration.

5 Data on samples prepared *ex situ* were measured at the Balder beamline at the MAX-IV laboratory.<sup>58</sup> The  
6 spectra were collected in transmission using a double crystal Si(311) monochromator, with acquisition  
7 times of approx. 2 min, thereafter a new position on the pellet was chosen, to minimize the risk of radiation  
8 damage. After data reduction, approx. 8 spectra were merged for better statistics.

9 XAS data were processed in Athena, and the data fitting was conducted in Artemis.<sup>48</sup> Linear combination  
10 analysis (LCA) fitting of XANES spectra (both *in situ* and *ex situ*) was carried out in Athena over the energy  
11 range -15 to +30 eV in regard to  $E_0$ . The phase content was restrained to values between 0 and 1, and the  
12 sum of the phases to 1. To obtain better statistics, data were merged, with every ten spectra below 450 °C  
13 where minimal changes were observed, and every second spectra above 450 °C to present data with a good  
14 time resolution. This procedure results in an uncertainty on the temperature below 450 °C of 45 °C and an  
15 uncertainty of 9 °C above.

## 16 **X-ray total scattering and pair distribution function analysis**

17 The *in situ* total scattering data were collected at the P21.1 ( $\lambda = 0.1204 \text{ \AA}$ ) beamline, while the *ex situ* data  
18 were measured at the P02.1<sup>59</sup> ( $\lambda = 0.2073 \text{ \AA}$ ) beamline, both at PETRAIII at the Deutsches Elektronen-  
19 Synchrotron (DESY) in Hamburg, Germany. Data were acquired on an amorphous silicon two-dimensional  
20 (2D) flat panel PerkinElmer XRD1621 detector ( $40 \times 40 \text{ cm}^2$  pixel size of  $200 \times 200 \text{ \mu m}^2$ ) in full ring  
21 configuration with an angular resolution ( $Q_{\text{max}}$ ) of  $25.5 \text{ \AA}^{-1}$  at P21.1 and on a VAREX XRD 4343CT  
22 detector ( $43 \times 43 \text{ cm}^2$  pixel size of  $150 \times 150 \text{ \mu m}^2$ ) with a  $Q_{\text{max}}$  of  $19.7 \text{ \AA}^{-1}$  at P02.1.

23 For the *in situ* pyrolysis, a custom-built capillary setup previously described<sup>60</sup> was used. To achieve a high  
24 transmission of X-rays, the ZIF-67 powder was packed in fused silica capillaries with an inner diameter of

1 0.7 mm and an outer diameter of 0.85 mm. The capillary was connected to the reactor using graphite ferrules  
2 and Swagelok fittings, allowing a flow of argon gas with 100 mL min<sup>-1</sup>. A heating ramp of 25 °C min<sup>-1</sup> was  
3 applied, using a hot air blower. As it was not possible to monitor the temperature inside the capillary during  
4 the pyrolysis experiment, a temperature calibration was performed prior to the experiment with a  
5 thermocouple. The reason for not repeating the experiment with a ramp of 3 °C min<sup>-1</sup> (matching the XAS  
6 experiment) was time restrictions at the synchrotron facilities. It is anticipated that at 3 °C min<sup>-1</sup> and at  
7 25 °C min<sup>-1</sup>, the mechanism of the structural evolution will be the same, however the onset temperature of  
8 the phase transition as well as the absolute extent of the transition will vary between the experiments.

9 *Ex situ* samples were measured in five blocks of 60 s dark followed by 5 x 60 s of exposure, thus a total  
10 measuring time of 5 min per sample. Samples were spun during the measurement.

11 The azimuthal integration and calibrations were performed with the Dioptas<sup>61</sup> and pyFAI (V0.20)<sup>62</sup>  
12 software. PDFgetX3<sup>63</sup> and xPDFsuite<sup>64</sup> were used for subtraction of the integrated intensities of an empty  
13 capillary and to obtain  $S(Q)$ ,  $F(Q)$ , and  $G(r)$  functions. A  $Q$ -range of 0.1-17.5 Å<sup>-1</sup> was used for the Fourier  
14 transformation of the *in situ* P21.1 data, and 0.1-19.2 Å<sup>-1</sup> for the *ex situ* data. In all cases, an  $R_{\text{poly}} = 1.1$  was  
15 applied. Data were collected on CeO<sub>2</sub> and LaB<sub>6</sub> standards to calibrate the distance from sample to detector,  
16 in addition to the instrumental  $Q_{\text{broad}}$  and  $Q_{\text{damp}}$  parameters. Data modelling was performed with DiffPy-  
17 CMI<sup>65</sup> and NMF analysis with the nmfMapping application on the PDFitc platform.<sup>66, 67</sup>

## 18 **Powder X-ray diffraction**

19 PXRD data were measured at room temperature on a Rigaku Smartlab diffractometer using Co K $\alpha_1$  and Co  
20 K $\alpha_2$  radiation ( $\lambda = 1.79$  Å). Parallel beam optics were used, and data were collected in an angular  $2\theta$  range  
21 of 5-90° on a D/TEX 250 strip detector. Rietveld refinement of the pristine ZIF-67 data was performed  
22 using the FullProf Software<sup>68</sup> to confirm the phase purity of the sample.

23

24

## 1 Scanning electron microscopy

2 Images were collected on a FEI-Nova Nano SEM 600 scanning electron microscope under high-vacuum  
3 conditions in field immersion mode through a lens detector (TLD). An accelerating voltage of 5.00 kV and  
4 a spot size of 4.0 were utilized. Samples were immobilized on aluminum supports with conductive carbon  
5 tape and coated with a 7 nm Pt layer using a Leica EM SCD 500.

6

## 7 Electrochemical OER

### 8 Electrode preparation

9 Toray carbon paper (CP) electrodes with a hydrophobic PTFE coating with an active geometric area of  
10  $1 \text{ cm}^2$  were utilized. The cast procedure adheres, with only minor modifications to that presented in our  
11 previous paper<sup>3</sup>. A Nafion ink was prepared with 6 mg of the pristine or pyrolyzed ZIF-67, 300  $\mu\text{L}$  of  
12 Nafion 5wt% solution in water and lower aliphatic alcohols, 450  $\mu\text{L}$  isopropanol, and 2250  $\mu\text{L}$  milliQ water.  
13 The ink was sonicated for 30 min, and 50  $\mu\text{L}$  was dropcast onto the CP, resulting in a catalyst load of  
14  $100 \mu\text{g cm}^{-2}$ . The electrodes were dried in an isopropanol atmosphere overnight.

### 15 Electrochemical characterization

16 A three-electrode system was employed for all electrochemical studies. Experiments were performed with  
17 a CHI660E potentiostat in an electrochemical batch H-cell with the cathodic and anodic chambers separated  
18 by a glass frit. The CP with catalyst ink deposited acted as the working electrode. A platinum mesh was  
19 employed as the counter electrode, while a leak-free Ag/AgCl (saturated KCl) electrode (ElectroCell LF-1)  
20 was used as reference electrode. The potential recorded with respect to Ag/AgCl was converted *versus* the  
21 reversible hydrogen electrode (RHE) through the following equation:

$$22 \quad E(V_{\text{RHE}}) = E^0_{\text{Ag/AgCl}}(V_{\text{NHE}}) + 0.059 \times \text{pH}$$

1 where  $E_{\text{Ag/AgCl}}^0 = 0.198 \text{ V}_{\text{NHE}}$ . A supporting aqueous electrolyte solution on 1 M  $\text{KOH}_{(\text{aq})}$  was saturated with  
2  $\text{N}_2$  (pH = 14) for 15 min before each experiment.

3 Linear sweep voltammetry (LSV) was performed with a scan rate of  $10 \text{ mV s}^{-1}$ . The activity was compared  
4 with that of the reference catalyst, *i.e.*  $\text{IrO}_2$  and a blank carbon paper. The polarization curves were  $iR$   
5 corrected, with a typical ohmic loss of  $3.3 \pm 0.3 \ \Omega$ . Chronopotentiometry was performed at  $10 \text{ mA cm}^{-2}$  for  
6 2 hours. The electrochemically active surface area (ECSA) was determined before and after  
7 chronopotentiometry for 2 hours. It was evaluated through cyclic voltammetry in the non-faradaic region  
8 at different scan rates to determine the double layer capacitance ( $C_{\text{DL}}$ ). The ECSA of the sample was then  
9 calculated according to the following equation:

$$10 \quad \text{ECSA} = C_{\text{DL}}/C_{\text{S}}$$

11 where  $C_{\text{S}}$  is the specific capacitance of the sample. This value is taken as  $0.04 \text{ mF cm}^{-2}$  in 1 M  $\text{KOH}_{(\text{aq})}$ .<sup>55</sup>

## 12 **Conflicts of interest**

13 There are no conflicts of interest to declare.

## 14 **Acknowledgements**

15 We gratefully acknowledge funding from the Carlsberg Foundation (CF19-0585 and CF14-0506) the  
16 Danish National Research Foundation (Carbon Dioxide Activation Center, DNRF 118), and DanScatt.  
17 Affiliation with Center for Integrated Materials research (iMAT) at Aarhus University is acknowledged.  
18 Work in the Billinge group was supported by the U.S. National Science Foundation through grant  
19 DMREF-1922234. We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association  
20 HGF, for the provision of experimental facilities. Parts of this research were carried out at the PETRA III  
21 beamline P02.1 and P21.1. We would like to thank Ann-Christin Dippel for assistance in using beamline  
22 P21.1. Beamtimes were allocated by an in-house contingent. Dr. Matthias S. Hvid is thanked for assistance  
23 during data collection at DESY. Likewise, we acknowledge the Diamond Light Source (UK) for beamtime

1 on B18 (proposal number SP22410), and Giannantonio Cibin is kindly acknowledged for his support at the  
2 beamline. We acknowledge the MAX IV Laboratory for time on the Balder beamline under Proposal  
3 20190489. Research conducted at MAX IV, a Swedish national user facility, is supported by the Swedish  
4 Research council under contract 2018-07152, the Swedish Governmental Agency for Innovation Systems  
5 under contract 2018-04969, and Formas under contract 2019-02496. Beamline scientist Justus Just is  
6 thanked for his assistance at the beamline.

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