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Herein we present non-noble metal single-atom catalysts (SACs) based on carbonized transition metal-doped zeolitic imidazolate frameworks (ZIFs) as stable and efficient electrocatalysts for the hydrogen evolution reaction in acidic media. In this work, earth-abundant metals are embedded in a porous N-rich carbon matrix by pyrolyzing metal-doped ZIF structures and characterized by spectroscopic, microscopic, and electrochemical methods. The complete synthesis of these high surface area SACs was carried out without any solvents and hence offers a promising route for a more sustainable catalyst production and industrial upscaling. As the best-performing catalyst, cobalt SAC illustrated already with a low cobalt loading of <0.3 at.% a substantial increase in activity with an overpotential of −322 mV for −10 mA cm−2, and high stability during electrolysis at −10 mA cm−2 for 12 h in acidic media, with only a small decrease of 33 mV to more negative potentials after the initiation period.

Introduction

Climate change caused by an increased carbon dioxide concentration in our atmosphere is one of the most crucial challenges of the 21st century.[1–3] To target this problem, a raising effort has been made to investigate alternative renewable energy carriers to replace fossil fuels.[4–6] Hydrogen emerged as a promising alternative due to its high gravimetric energy density.[7–11] Besides replacing fossil fuels, hydrogen can also be used as feedstock in industrial processes, such as steel reforming, reducing carbon dioxide emissions of the process, and thus paving the way for a green and sustainable society.[12] In contrast to the commonly used steam reforming and water-gas shift reaction, which simultaneously produce hydrogen and carbon dioxide, an environmentally friendly and carbon-neutral method to produce hydrogen is electrochemical water splitting with electricity provided by renewable energy sources, such as wind or solar power.[7,9,10,13–18] Unfortunately, to this date, electrochemical water splitting is unattractive due to high process costs, compared to e.g. steam reforming,[7,9,19] hampering the commercialization and up-scaling of electrochemical water-splitting devices. One reason for the high process costs are the expensive catalysts used, which are required to reduce the potential needed for the water-splitting reaction.[20] Currently, platinum is known to be the most efficient catalyst for the hydrogen evolution reaction (HER).[21,22] Therefore, rising effort is made to substitute raw and expensive metals with more abundant and affordable materials.[1,23–26] Especially transition metal-based catalysts like phosphides, sulphides, and carbides showed promising behavior.[24,27–31] Unfortunately, some of those catalysts have limited stability in aqueous media.[31] Furthermore, only atoms on the surfaces exposed to the electrolyte can act as catalytic active sites. Metal atoms in the bulk material are hence inactive and unfavorable.[32] A promising class of catalysts to overcome this throwback are single-atom catalysts (SACs), which are metal and nitrogen co-doped porous carbon materials with the metal atomically dispersed in the carbon matrix.[33] Those catalysts are usually synthesized by pyrolyzing a mixture of C-, N- and metal precursors,[34–38] transition metal complexes,[39–41] or metal–organic frameworks (MOFs).[1,42–45] Unfortunately, these synthesis processes often require multiple steps,[11,32,34,39,43] the use of organic solvents,[32,34,39,46] and/or acid treatment afterwards,[1,34,35,39,47] which might hamper the industrial production of those catalysts.[48,49]
One popular subclass of MOFs is zeolitic imidazolate frameworks (ZIFs), in which imidazole linkers coordinate to the metal cations.\textsuperscript{50,51} Compared to other MOFs, ZIFs are known to have exceptional chemical and thermal stabilities.\textsuperscript{50} Especially carbonized ZIF-8 structures are due to their high surface area in combination with high nitrogen content a promising material for SACs.\textsuperscript{52}

In the here presented work, we synthesized ZIF-8 structures doped with different earth-abundant metals (Co, Ni, Fe, Mn) and subsequently carbonized them to produce transition metal SACs embedded in a porous N-doped carbon matrix. The SAC materials were drop casted on a carbon-based gas diffusion layer (GDL) and evaluated for their activity and stability towards the HER in acidic media. The cobalt SAC especially showed high activity and stability even at low Co-loading. Since the entire synthesis process solely consists of two mixing and two heating processes and is free of solvents and acid treatment afterwards, it is an interesting approach for industrial upscaling of low-cost SACs.

Results and Discussion

Characterization of the as-synthesized materials

After pyrolysis, powder x-ray diffraction (PXRD) studies were implemented to check for the presence of metal-based nanoparticles in the material. The diffractograms showed only minor peaks at 20°, 26°, and 44°, which likely originate from graphene (JCPDS 75-2078), graphene oxide, and graphite (Figure 1).\textsuperscript{35,41,46,51,54} The peak at 26° in C–Co-ZIF-8, C–Ni-ZIF-8, and C–Fe-ZIF-8 originate from the (002) plane of graphitized carbon with the intensity for Fe > Ni > Co. This can be explained by the known ability of Fe, Ni, and Co to graphitize carbon.\textsuperscript{55} No other peaks were detected in the diffractograms, suggesting the absence of a significant amount of crystalline metal-based nanoparticles in all compounds and indicating a successful synthesis of majorly single-metal atoms distributed in the amorphous carbon matrix. The synthesis of ZIF-8 before pyrolysis was confirmed by PXRD of the undoped compound where only ZnO and 2-MeIm were used in the solid-state synthesis (Figure S2) (JCPDS 00-062-1030).

Scanning electron microscopy (SEM) was used to investigate the morphology and nanostructures of the as-synthesized materials. As illustrated in Figure 2a and Figures S3–S7, all catalysts exhibited a non-uniform particle size with random shapes. Notably, high amounts of carbon nanotubes (CNTs) were detected in C–Co-ZIF-8 and C–Ni-ZIF-8 (Figure S4, Figure S5). In contrast, no CNTs were observed in C–Fe-ZIF-8, C–Mn-ZIF-8, and C-ZIF-8. The presence of CNTs in C–Ni-ZIF-8 and C–Co-ZIF-8 explains the graphitic carbon peak detected at 26° in Figure 1. However, since C–Fe-ZIF-8 exhibits the highest intensity for said peak but no CNTs were detected, the graphitized carbon might be present as graphite or graphene sheets.

![Figure 1. PXRD analysis of the as-synthesized materials after carbonization of the transition metal-doped ZIF-8 structures (black: undoped, red: Co-doped, blue: Ni-doped, green: Fe-doped, purple: Mn-doped). No reflexes corresponding to metal-based nanoparticles were found. The detected peaks were attributed to C-based materials, such as graphene (JCPDS 75–2078).](image1.png)

![Figure 2. SEM analysis of the as-synthesized C–Co–ZIF-8. (a) Secondary electron (SE) image of the material with random morphology and nanotubes present. (b) Overlay of SE image of (a) with cobalt EDX mapping. Orange spots represent the presence of homogeneously dispersed Co within the sample.](image2.png)
Energy dispersive X-ray spectroscopy (EDX) mapping revealed a homogeneous dispersion of the different elements in the material (Figures S8–S12). Representative for all materials, the homogeneous dispersion of the doping metal within the N-doped porous carbon matrix is shown in Figure 2b for C-Co-ZIF-8. No notable cluster of doping metal on a macroscopic scale was observed in any material. The elements detected by EDX mapping were Si from the wafer, C, N, O, Zn, and the doping metal, suggesting a successful integration of all doping elements into the matrix. X-ray photoelectron spectroscopy (XPS) below confirmed and quantified the atomic concentration of the different elements in the samples. Transmission electron microscopy (TEM) was utilized to probe the presence of nanoparticles in C–Co-ZIF-8 on the nanoscale. With conventional TEM in bright field mode (BF) a to a high extent amorphous carbon material was detected (Figure S13a). Only at higher resolutions, a few small crystalline regions indicated by diffraction contrast were observed in some areas, which implied the formation of a few small nanoparticles (Figure S13b and c).

EDX mapping in scanning TEM (STEM) mode has shown a homogeneous dispersion of Co in the matrix throughout the whole material (Figure 3), supporting the hypothesis of predominantly single-atoms embedded in an N-doped amorphous carbon matrix (Figure S14, Figure S15). However, it should be noted that in areas with diffraction contrast, some were detected to be Co-rich, indicating the possible formation of a few cobalt-based nanoparticles (Figure S15). As nanoparticles are unstable in acidic conditions, this might explain the loss of Co during operation as discussed below. Nevertheless, selected area electron diffraction (SAED) and fast Fourier transform (FFT) of high-resolution BF images were employed to further probe the material on the presence of crystalline phases. As visible in Figure 3d and Figures S16–S18, no sharp defined diffraction rings were detected, suggesting the absence of a significant number and size of nanoparticles. The observed halos likely originate from carbon structures, in agreement with reflexes observed in XRD. The TEM analysis thus can be rationalized with the transition metal majorly being present in a single atomic nature homogeneously dispersed in the N-doped carbon matrix with the formation of nanoparticles being possible, but an exception.

X-ray photoelectron spectroscopy (XPS) analysis of the as-synthesized materials confirmed the presence of C, N, O, Zn, and the corresponding doping metal in all samples, as shown for C–Co-ZIF-8 in Figure 4a, corroborating the EDX analyses by...
SEM and TEM above. All high-resolution spectra are charge corrected versus adventitious C 1s at 284.8 eV. The concentration of the doping metal was quantified as 0.28 at.% Co, 0.30 at.% Ni, 0.23 at.% Fe, and 0.33 at.% Mn, thus presenting a material with a very low metal loading. The complete compositions based on the high-resolution spectra (Figures S19–S23) are given in Table S1. The detection of Zn originates from the incomplete evaporation of the Zn nodes from the parent ZIF-8 structure. It should be noted that the initial molar ratio of Zn to doping metal in the synthesis was 98:2. XPS analysis after the carbonization shows a similar atomic concentration between Zn and the doping metal and hence corroborates a substantial removal of Zn. All transition metal 2p\textsubscript{x-y} peaks showed the absence of metallic contribution above the detection limit, indicating the presence of metals in higher oxidation states, possibly preserved in the initial +II oxidation state from the synthesis. The O 1s and C 1s spectra showed no detectable amount of metal oxides or carbides, respectively, corroborating the XRD results and implying that the metal must mainly be bound to other elements. The high-resolution N 1s spectra in Figure 4b could be deconvolved in four contributions at (398.6 ± 0.1) eV, (399.4 ± 0.1) eV, (401.1 ± 0.0) eV, and (402.4 ± 0.2) eV, which can be rationalized with the presence of pyridinic N, pyrrolic N, graphitic N and N-oxides, respectively (Table S2). The detected binding energies for N 1s are in agreement with previously reported values, however, the exact binding energy for metal N is difficult to determine. Due to the low metal loading its contribution can be expected to be small and additionally overlapping with the dominating pyridinic and the pyrrolic peak. Since metal carbides and metal oxides were ruled out by the missing contribution in the high-resolution O 1s and C 1s spectra, the pyridinic, pyrrolic, and graphitic N are likely the sites to which the individual metal atoms are bound. In addition, no metallic peak could be observed in the corresponding metal 2p\textsubscript{x-y} spectra above the detection limit, ruling out a significant metallic nanoparticle formation and corroborating the XRD results above.

As only a few single nanoparticles were observed by TEM, while neither XPS, XRD nor SEM could provide any evidence for a significant presence of nanoparticles, it is hypothesized that there might be only a small number of nanoparticles present in the material and that the doping metal is mainly embedded in the carbon matrix as SAC.

The surface area of the carbonized structures was calculated by Brunauer-Emmet-Teller theory (BET) of the nitrogen adsorption-desorption isotherms and was detected in the range of 1217–846 m\textsuperscript{2}g\textsuperscript{-1} with C-ZIF-8 > C–Co-ZIF-8 > C–Mn-ZIF-8 > C–Ni-ZIF-8 > C–Fe-ZIF-8 (Table S3). It confirmed a high surface area and microporosity for all carbonized materials. However, it also illustrated a loss of surface area by the substitution of Zn\textsuperscript{2+} with the doping metals. Tang et al. reported a significant decrease in the surface area of the carbonized ZIF after fully substituting Zn\textsuperscript{2+} with Co\textsuperscript{2+}, corroborating this observation. The hysteresis present in the Co, Ni, Fe, and Mn SACs indicated likely an additional mesoporosity in these compounds (Figure S24).

**Electrochemical analysis**

Before detecting the catalytic response, each electrode was equilibrated by cyclic voltammetry (CV) with a scan rate of 50 mV s\textsuperscript{-1} until the voltammograms showed a stable response. The CVs probing the catalytic activity of the electrodes are shown in Figure 5a. Even though the cyclic voltammograms of the fresh C-ZIF-8 were stable, the forward and reverse scan crossed at approximately −305 mV, which was not visible for any other material and also not after the C-ZIF-8 ink aged for one day, which simultaneously decreased its activity drastically. C–Co-ZIF-8 showed the highest activity with an overpotential of 0.15 V, while both Co SAC showed the highest activity and good stability.

![Figure 5](image-url)
322 mV for $-10 \text{ mA cm}^{-2}$, illustrating a clear improvement in the catalytic activity compared to the parent – aged and fresh – C-ZIF-8 material. Noteworthy, this significant enhancement of activity already happened for a very low loading of approximately 1.32 wt%, which is a strong contrast to the reference Pt/C catalyst with 40 wt% metal. In comparison, the Co-SAC presented by Sa and Park et al.\(^{29}\) reported a similar overpotential of approximately 219 mV for a current density of $-10 \text{ mA cm}^{-2}$ with a higher Co-loading on the working electrode (11.2 $\mu$g cm$^{-2}$ vs. 6.6 $\mu$g cm$^{-2}$). However, the analysis of Co-loading and the electrodes used differ, so the comparison should be taken with care. C–Fe-ZIF-8, C–Mn-ZIF-8, and C–Ni-ZIF-8 with overpotentials for $-10 \text{ mA cm}^{-2}$ of 525 mV, 598 mV, and 605 mV, respectively, did not improve the catalytic activity compared to the fresh C-ZIF-8, but significantly compared to the aged C-ZIF-8. Interestingly, the presence of CNTs did not seem to have a significant influence on the catalytic activity as observed for the performance of C–Ni-ZIF-8 with CNTs compared to C–Mn-ZIF-8 without. Liang et al.\(^{34}\) reported an overpotential of 133 mV at $-10 \text{ mA cm}^{-2}$ for their Co-SAC with an even lower Co loading and a similar BET compared to our material. However, also the activity and the performance of the Mn, Fe, and Ni metal centers for HER in their work are different from ours. A possible reason might be the synthesis route leading to the SAC.

The positive HER onset and overpotential for the Pt/C catalyst in our work was attributed to the absence of 1 atm. hydrogen during the cycle, shifting the thermodynamic potential for hydrogen evolution calculated by the Nernst equation to more positive values. This makes comparison to other publications more challenging, however, the comparison among the catalysts used in this work remains valid.

Tafel slope analysis of the fully iR compensated forward scan confirmed with the slope for Co < Fe < Ni < Mn the highest activity for C–Co-ZIF-8 (Figure S25). With slopes of 105 $-156 \text{ mV dec}^{-1}$, all catalysts indicate the Volmer step as the rate-limiting step. Such high slopes agree with previously reported values of carbonized metal-doped ZIF-8 structures.\(^{42}\) Sa et al.\(^{38}\) proposed based on the work of Tilak and Chen\(^{37}\) that the surface coverage of active sites might explain deviations in the Tafel slopes from the widely known slopes of 120 mV dec$^{-1}$, 40 mV dec$^{-1}$, and 30 mV dec$^{-1}$ for the Volmer, Heyrovsky, and Tafel step, respectively.\(^{18,58}\) Generally, having SAC, the lowest Tafel slope obtained would be 40 mV dec$^{-1}$ for the Volmer-Heyrovsky mechanism. For the Volmer-Tafel mechanism associated with a slope of 30 mV dec$^{-1}$, two adsorbed hydrogen atoms on the active sites would be needed to be close together to recombine. In SAC materials the active sites are expected to be too far away from each other to enable this mechanism, assuming that the metal is the adsorption site.\(^{59}\)

The electrochemical stability of the catalysts was evaluated by chronopotentiometry (CP) at $-10 \text{ mA cm}^{-2}$ for several hours (Figure 5b). The fresh C-ZIF-8 showed a stable behavior over the whole 2 h tested, suggesting an inert matrix. The drop to a more negative potential in the first 30 minutes of the measurement was attributed to the formation of hydrogen bubbles on the electrode, which imposes diffusion limitations and deactivation of active sites. As no doping metal was used, leaching of the active sites is not possible and the loss of active sites was ruled out by an unchanged double-layer capacitance described below. After the initial drop, the potential remained almost constant during the time measured. The shift to more negative potentials during CP for the metal-doped C-ZIF-8 structures was attributed to the deactivation of active sites due to bubble formation as for the parent C-ZIF-8 but also to an irreversible degradation mechanism of the electrode and hence serves as an indicator to evaluate the electrochemical stability of the catalysts. High stability and activity were observed for C–Co-ZIF-8, which overall potential drop was only $\Delta E = -17 \text{ mV}$ after 4 hours at $-10 \text{ mA cm}^{-2}$ compared to the detected potential after 30 minutes, showing in accordance with CV above and galvanostatic electrochemical impedance spectroscopy (GEIS) below the best performance of the tested materials. After 12 h the overall potential shift for $-10 \text{ mA cm}^{-2}$ was $\Delta E = -33 \text{ mV}$ compared to after 30 minutes, meaning that after 4 hours the potential shifted in the following 8 hours only by $-16 \text{ mV}$. This strongly suggested that the major irreversible loss of activity happens at the very beginning of the exposure and can be rationalized with the leaching of metal nanoparticles, as indicated by TEM in the as-synthesized C–Co-ZIF-8. Leaching of the single atom distributed metals seems unlikely since it would cause a continuous loss of potential in the CP, more severe than what was observed. In addition, the required potential in the CP would approach a potential similar to that of undoped C–ZIF–8. C–Ni-ZIF-8 and C–Fe–ZIF-8 illustrated a similar shift with both $\Delta E = -13 \text{ mV}$ during 4 hours of CP. The assumption of stable SACs is further strengthened by the change in electrochemical surface area and atomic concentration elaborated below. Since C–Fe–ZIF-8 and C–Ni–ZIF–8 exhibited a similar trend as C–Co–ZIF–8, it is likely that also in those materials small nanoparticles were present. Despite having the largest surface area among the tested carbonized metal-doped ZIF-8 structures as detected by BET, and the highest concentration of doping metal as detected by XPS, C–Mn–ZIF–8 showed to be unsuitable for catalyzing the HER in this condition. The initial catalytic activity of this compound was similar to C–Ni–ZIF–8, but in CP differed quite substantially. As the same electrodes were used for the electrochemical analysis and the CP was carried out after CV, this strong decrease in performance can be explained by the chemical instability of C–Mn–ZIF–8, which is further strengthened by the continuous decrease in activity observed in the CP.

In order to detect the charge transfer resistances ($R_{CT}$) of the different materials, GEIS was used at $-10 \text{ mA cm}^{-2}$ and on the catalytic wave at $-40 \text{ mA cm}^{-2}$. The Nyquist plots and the corresponding charge transfer resistances are given in Figure S26 and Table S4. C–Co–ZIF–8 showed the lowest $R_{CT}$ for both applied current densities compared to all other materials, indicating the fastest electron transfer for this catalyst and supporting the enhanced activity detected in the other electrochemical characterization techniques. At $-10 \text{ mA cm}^{-2}$, C–Co–ZIF–8 exhibited with 9.0 $\Omega$ a significantly reduced resistance in comparison to C–ZIF–8 with 14.4 $\Omega$. At $-40 \text{ mA cm}^{-2}$, the charge transfer resistance for C–Co–ZIF–8...
further decreased to 2.1 Ω. All metal doping lowered the $R_{CT}$ at the beginning of the catalytic wave at $-10 \text{ mA cm}^{-2}$ compared to the parent C–ZIF-8. The aged C–ZIF-8 was used for this experiment to exclude influences of the activation phenomenon described above for the fresh C–ZIF-8 electrode. The decreasing $R_{CT}$ at $-10 \text{ mA cm}^{-2}$ with Mn, Ni, Fe to Co doping agrees with the decreased overpotential detected in the CVs. On the catalytic wave at $-40 \text{ mA cm}^{-2}$, all electrodes exhibited a decreased $R_{CT}$ compared to at $-10 \text{ mA cm}^{-2}$. However, only Co doping lowered the resistance compared to the parent C–ZIF-8, even though the applied potentials for all other metal-doped C–ZIF-8 were below the parent C–ZIF-8. This suggests at high current densities, that charge transfer resistance may only play a minor role in the overall activity of the catalyst.

Post catalytic analysis

The stability assessment based on CP was further corroborated by the analysis of the electrochemical surface area (ECISA), XPS, XRD, and SEM analysis after catalysis as shown below.

To follow the change in ECSA, the double-layer capacitance ($C_{dl}$) was determined by cycling in the non-faradaic regime before and after the CP exposure at different scan rates (Figure S27–S31). As listed in Table S5, fresh C–ZIF-8 had an unaltered $C_{dl}$ indicating an inert material during the CP exposure. All metal-doped and carbonized ZIF-8 structures exhibited a decrease in double-layer capacitance during the CP. Assuming an unchanged specific capacitance for all materials before and after exposure, this would be equivalent to a loss of surface area, which can be explained by minor nanoparticles getting dissolved during the electrochemical exposure. This is further corroborated by the XPS analysis below, which detected a similar loss of metal for Co and Fe and a higher stability of Ni, which could be reflected by a similar loss in electrochemical surface area for C–Co–ZIF-8 and C–Fe–ZIF-8 and a larger remaining area for C–Ni–ZIF-8. However, with a remaining $C_{dl}$ of 83% and above, the presence of a large surface area after CP was verified for all tested catalysts. The high remaining surface area of C–Mn–ZIF-8 can be rationalized by the shorter CP exposure compared to the other catalysts.

To investigate the chemical stability of the catalyst in the electrolyte without any applied bias, C–Co–ZIF-8, C–Fe–ZIF-8, and C–Ni–ZIF-8 powders were immersed in 0.5 M sulfuric acid for one week. After collecting, washing, and drying, the elemental composition was analyzed by XPS (Figure S32–S34) and calculated in Table S6. Assuming that the carbon and nitrogen content was not affected by the exposure to sulfuric acid, the metal/carbon and metal/nitrogen ratios before and after exposure were compared (Table S7). A rather unchanged ratio for C–Ni–ZIF-8 was detected, corroborating its higher stability proposed by ECSA. However, the slight deviations in proposed stabilities by ECSA and XPS for this material could be explained by either a reorganization of the material during the electrochemical exposure, leading to a decreased surface area without a compositional change, or the dissolution of Ni being promoted by an applied electrochemical load. The metal/C and metal/N ratio after exposure for C–Co–ZIF-8 and C–Fe–ZIF-8 decreased to 70 – 75% of the original ratio, agreeing with the similar decrease in surface area during the CP for those catalysts as described above. This decrease is attributed to the instability of nanoparticles in the acidic electrolyte. Furthermore, comparing C–Ni–ZIF-8 and C–Fe–ZIF-8 leads to very important conclusions. Despite C–Ni–ZIF-8 having visible CNTs, C–Fe–ZIF-8 exhibits higher activity as observed with the lower overpotential in the CV, the lower applied potential in CP, and the lower $R_{CT}$ as detected in GEIS, indicating that the presence of CNTs had no major contribution to the activity. XPS analysis on the C–Co–ZIF-8 electrode before and after electrolysis confirmed the leaching of Co during the electrochemical exposure (Figure S35). After catalysis the Co/N ratio decreased to approximately 51%, indicating that the redeposition of dissolved cobalt from the nanoparticles onto the electrode during operation is unlikely (Table S9). However, it should be noted that the dominant fluorine peak from the binder makes the exact quantification of Co uncertain, but overall agrees with a loss of Co during the testing.

After the electrochemical exposure, XRD analysis of the C–Co–ZIF-8 electrode showed no change in the diffraction pattern compared to before the electrochemical tests, suggesting no major restructuring during the electrochemical experiments (Figure S36). The only signals detected are carbon-based (graphite, graphene, graphene oxide, polytetrafluoroethylene).

In addition, SEM analysis on the working electrode with C–Co–ZIF-8 before and after an accelerated durability test with electrolysis at $-20 \text{ mA cm}^{-2}$ for 3.75 hours corroborates the picture of a stable material (Figure S37). The overall morphology shows only minor changes in the surface structure; however, it is unclear if those differences are caused by catalysis or by the volume change of the Nafion binder used upon swelling and drying during the electrochemical exposure and before the SEM analysis, respectively.

Conclusion

The synthesis of SAC and the improvement of the catalytic activity for HER by substituting Zn$^{2+}$ with other transition elements during the ZIF-8 synthesis was presented. CV, Tafel slope analysis, CP, and charge transfer resistances confirmed the enhancement of the activity for HER with Co > Fe > Ni > Mn. The lowest overpotential and Tafel slope for HER detected in CV for C–Co–ZIF-8 in combination with the lowest charge transfer resistances determined by GEIS at $-10 \text{ mA cm}^{-2}$ and $-40 \text{ mA cm}^{-2}$, the lowest applied potential for the CP at $-10 \text{ mA cm}^{-2}$, and the high stability during 12 hours of electrochemical loading paint a picture of a very potent electro-catalyst. The straightforward synthesis of the material without the need of solvents and purification steps presents an interesting way of producing primarily SAC on a larger scale ($\approx 10 \text{ g}$ before carbonization). With EDX in SEM and TEM, a mostly homogeneous dispersed doping metal was verified, indicating SAC being present to a high extent. This assumption
was supported by XRD, XPS, SEM, and TEM which could not detect the presence of a significant amount of nanoparticles. Furthermore, those formed were able to be dissolved in situ, avoiding an acid treatment with HF. After the initial removal of nanoparticles, the material illustrated a stable behavior under an electrochemical load for several hours. Even at very low loading, the activity was significantly enhanced and can be further optimized by increasing the amount of doping metal. With slight variations in the synthesis procedure as the mixing time and parameters, could further reduce the formation of nanoparticles while simultaneously increasing the activity.

Experimental Section

Materials

All materials were used as received without any further purification. Zinc oxide (99.9 %, metals basis, ~200 mesh powder), 2-methylimidazole (97 %), iron(II) oxalate dihydrate (99 %), nickel(II) oxalate dihydrate, cobalt(II) oxalate dihydrate (reagent grade) and manganese(II) oxalate dihydrate (Mn 30 % min) were provided by Alfa Aesar. 2-propanol (AnalaR NORMAPUR, Reag. Ph.Eur., Reag. USP, ACS) was purchased by VWR, Nafion perfluorinated resin solution (5 wt.% in lower aliphatic alcohols and water, contains 15–20 % water) and platinum on graphite (carbonized 40 wt.%) by Sigma Aldrich, and sulfuric acid solution (FLUKA, 0.5 M, 1.0 N) by Honeywell. Deionized water was obtained by a PURELAB Chorus system from ELGA LabWater.

Synthesis

The synthesis of the carbonized transition metal doped ZIF-8 structures was inspired by Liu et al. In short, ZnO was mixed with the desired metal oxalate dihydrate and excess 2-methylimidazole (2-Melm) in a molar ratio of 0.98:0.02:2.6 in a tube mill. The powder mixture was transferred into a glass in a polyphenyl-lined stainless-steel autoclave and heated up to 220 °C, where it was held for 10 hours. To advocate for the possibility to upscale this process, a total mass of ~10 g was synthesized for each compound. The synthesized metal-doped ZIF-8 structures were crushed by tube milling and carbonized at 1000 °C in an argon atmosphere leading to the carbonized metal-doped ZIF-8 structures, from here on called C–Co–ZIF-8, C–Fe–ZIF-8, C–Ni–ZIF-8, and C–Mn–ZIF-8, depending on the doping metal. As reference also an undoped carbonized ZIF-8 (C–ZIF-8) with 100 mol% ZnO was synthesized accordingly.

Catalyst characterization

For powder X-ray diffraction (PXRD) the material was analyzed with a Bruker D8 Advanced operating with Cu Kα radiation (λ = 0.154 nm). Diffractograms were recorded in the 2θ range from 5° to 80°. A step size of 0.02° with 0.98 s per step was used. The acquired diffractograms were analyzed using the GSAS software. High-resolution scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) were performed with a ZEISS LEO 1530 with a Schottky FEG and acceleration voltages of 20 keV. For imaging, the Inlens secondary electron detector was used with the software SmartSEM (Version 5.07). For EDX analysis the Oxford Instruments X-MaxN with the corresponding AZTec software (Version 3.3) was used with the recommended working distance of 8.5 mm. During the revision, a Hitachi S-4500 with a secondary electron detector and the Quartz PCI software was used for analyzing the surface of the working electrode before and after electrolys. Transmission electron microscopy (TEM) was performed with a TECNAI 30 G2 and a Titan ETEM 300 G2 with an acceleration voltage of 300 kV. For EDX analysis an XFlash 6–60 detector from Bruker was used. For treatment of the acquired images ImageJ and INCA have been used. X-ray photoelectron spectroscopy was acquired with a Kratos Axis ULTRA DLD instrument with monochromatic Al Kα radiation (1486.69 eV). The survey spectra were taken with a beam power of 150 W, 2 sweeps, a dwell time of 0.1 s, 1 eV step size, 160 eV pass energy, and no charge neutralization. High-resolution spectra were acquired with the same beam power, 6 – 40 sweeps (details in the ESI), 0.05 eV step size, 0.2 s dwell time, a pass energy of 40 eV, and no charge neutralization, except for the analysis on the electrodes. The area of analysis was always 300 μm × 700 μm. The spectra were analyzed with CasaXPS Version 2.3.19PR1.0.0([48] Bruiner-Emmett-Teller surface area (BET) analysis was acquired with NOVApoint LX2. The nitrogen adsorption and desorption isotherms were recorded at 77 K. Prior to the measurement the samples were degassed under vacuum at 300 °C for 1 h. For the electrochemical analysis, the carbonized ZIF-8 structures were mixed into an ink and drop casted on a hot GDL (SGL Carbon Sigraget 28 BC). The drop casting volume was chosen to achieve a catalyst material mass loading of 0.5 mg cm⁻². The prepared electrode was tested in a three-electrode half-cell configuration in 0.5 M sulfuric acid at 20 °C against a commercial normal hydrogen reference electrode (NHE) (Gaskatel HydroFlex), which redox potential was calibrated versus Ag/AgCl (sat. KCl) reference electrodes. A carbon rod was used as the counter electrode. The whole setup was similar to the one used by Le Goff et al. The Bio-Lego SAS SP-300 potentiostat was used for the electrochemical measurement with the EC-Lab software V11.30. The electrolyte was bubbled prior to and during the electrochemical measurements with N₂ through a PTFE tube to remove oxygen in the solution. For each working electrode, the electrolyte was renewed, and the half-cell as well as all components in contact with the electrolyte were rinsed with deionized water. To probe the stability of the catalytic material in the electrolyte, C–Co–ZIF-8, C–Fe–ZIF-8, and C–Ni–ZIF-8 powder were exposed to 0.5 M sulfuric acid for one week and investigated with XPS. A more detailed description is given in the ESI.

Author Contributions

RD and BJ conceived and designed the study. RD synthesized and analyzed the materials electrochemically, with SEM and EDX. BJ contributed with XRD and BET measurements, JL and BV performed the XPS and TEM experiments, respectively. RD analyzed the data, FO contributed to the formulation and the deposition of the catalytic ink, and RD wrote the manuscript. ES contributed with XPS. A more detailed description is given in the ESI.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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