Active-Site Imprinting: Preparation of Fe–N–C Catalysts from Zinc Ion–Templed Ionothermal Nitrogen-Doped Carbons

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Atomically dispersed Fe–N–C catalysts are considered the most promising precious-metal-free alternative to state-of-the-art Pt-based oxygen reduction electrocatalysts for proton-exchange membrane fuel cells. The exceptional progress in the field of research in the last ≈30 years is currently limited by the moderate active site density that can be obtained. Behind this stands the dilemma of metastability of the desired FeN₄ sites at the high temperatures that are believed to be a requirement for their formation. It is herein shown that Zn²⁺ ions can be utilized in the novel concept of active-site imprinting based on a pyrolytic template ion reaction throughout the formation of nitrogen-doped carbons. As obtained atomically dispersed Zn–N–Cs comprising ZnN₄ sites as well as metal-free N₄ sites can be utilized for the coordination of Fe²⁺ and Fe³⁺ ions to form atomically dispersed Fe–N–C with Fe loadings as high as 3.12 wt%. The Fe–N–Cs are active electrocatalysts for the oxygen reduction reaction in acidic media with an onset potential of E₀ = 0.85 V versus RHE in 0.1 M HClO₄. Identical location atomic resolution transmission electron microscopy imaging, as well as in situ electrochemical flow cell coupled to inductively coupled plasma mass spectrometry measurements, is employed to directly prove the concept of the active-site imprinting approach.

1. Introduction

Our planet is currently facing many environmental issues such as abuse of resources and vast emissions of climate-active gases. In order to move toward a more green society, electrochemical systems are promising alternatives for coal-based devices, especially in the automotive field, where sales of light electric vehicles (battery electric vehicles and plug-in hybrid electric vehicles) are politically pushed and increasing exponentially.[1] Vehicles based on proton-exchange-membrane fuel cells (PEMFCs) have the potential to surpass the limitations of battery-based ones, especially, regarding the driving range. Unfortunately, the mass commercialization of this technology is hampered by the limited availability and high cost of Pt, which is required to speed up the anodic and cathodic reactions happening in a PEMFC.[2,3] Since ≈4 times more Pt is required on the cathode than at the anode side, the development of cathode materials containing low Pt amount is a promising way to reduce costs. Unfortunately, low-Pt cathode materials suffer from other limitations, such as losses due to mass transport,[4] also, when the Pt content is reduced below 100 µg cm⁻², the cost of other components rises.[1] For these reasons, completely replacing the Pt at the cathode side is a reasonable and promising way to go.

In the last 10 years, platinum-group-metal-free (PGM-free) catalysts for the oxygen reduction reaction (ORR) have drawn...
the attention of many research groups all over the world. Since it has been shown that bioinspired metal-nitrogen-doped-carbon (M–N–C, M = Fe, Co) catalysts could meet the requirements for real application in PEMFCs,[8–7] the number of publications on this topic has grown considerably and even commercialization of a PGM-free cathode-based fuel cell was recently reported.[8]

State-of-the-art synthetic protocols involve the mixing of Fe, N, and C precursors followed by pyrolysis. Despite the impressively optimized catalyst preparation, leading to very active catalysts, the procedure is intrinsically limited, since the desired atomically dispersed FeN₄ sites are metastable in the temperature range of their thermochemical formation. This dilemma limits the concentration of FeN₄ active sites, since higher iron precursor concentrations trigger the condensation of iron atoms that are produced by carbothermal reduction. Accompanied by support degradation,[9] eventually nanoparticles of elemental iron, iron carbide, and iron nitride are formed, which have been shown to be poorly ORR active compared to FeN₄ moieties (Scheme 1A).[10,11] For this reason, multiple processing steps are required to prepare phase pure catalysts containing FeN₄ sites only. Although the challenge of scalability is not always taken in account, some recent approaches to limit the ion mobility show very promising results; however, since all pyrolytic approaches are based on kinetic stabilization only, the active site density is usually pretty low, with Fe contents typically not exceeding 3 wt%.[12–14]

In more than 30 years of research, no successful preparation of ORR-active Fe–N–Cs was reported based on the coordination of iron to metal-free nitrogen-doped carbons (NDCs). Obviously, the likelihood of randomly occurring N₄ coordination sites is very low, so that Fe ions will, normally, only be loosely bound to the NDC surface (Scheme 1B). Recently, our group was able to decouple the synthesis of the carbon scaffold, acting as a solid-state ligand, from the formation of the active sites using a newly developed strategy involving Mg²⁺ as an imprinting metal ion throughout carbonization, analogous to the template ion reaction used in the preparation of macrocycles.[15] The preparation of highly porous Mg–N–C was followed by a low-temperature wet-chemical coordination step to form square-planar FeN₄ sites by either metalation (Equation (1)), transmetalation (Equation (2)), or both.[16] By which reaction the active sites are generated remains an open question to the scientific community.

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\text{Fe}^{3+} + \text{“N}_4^- \rightarrow \text{“Fe}^{0} \text{N}_4^-
\]

(1)

\[
\text{Fe}^{3+} + \text{“Mg}^{2+} \text{N}_4^- \rightarrow \text{“Fe}^{2+} \text{N}_4^- + \text{Mg}^{2+}
\]

(2)

At temperatures typically chosen for the pyrolytic synthesis, the reduction of Mg²⁺ is thermodynamically not favored; hence, this method has a great potential to increase the active sites’ density by avoiding thermally induced side reactions.

The inspiration for the research on Fe–N–C materials lies in the oxygen-binding property of the FeN₄ motif in the naturally occurring protoporphyrin IX. The coordination of an FeN₄ moiety to Zn ion-coordinated N₄ macrocycles (protoporphyrin) is exemplified by the physiological condition of the erythropoetic protoporphyria disease. D) The synthetic approach of active-site imprinting using Zn as imprinting metal and transmetalation toward Fe–N–Cs. E) The conceptual analogy between the synthesis of Fe phthalocyanine via template-ion-assisted formation of Zn phthalocyanine followed by transmetalation and the herein presented synthetic solid-state chemistry approach.

Scheme 1. Cartoon illustrating A) the dilemma of metastability of FeN₄ sites at pyrolytic conditions, and B) the unlikelihood to form FeN₄ sites by Fe ion coordination to metal-free NDCs. C) The natural abundance of Zn coordinated N₄ macrocycles (protoporphyrin) is exemplified by the physiological condition of the erythropoetic protoporphyria disease. D) The synthetic approach of active-site imprinting using Zn as imprinting metal and transmetalation toward Fe–N–Cs. E) The conceptual analogy between the synthesis of Fe phthalocyanine via template-ion-assisted formation of Zn phthalocyanine followed by transmetalation and the herein presented synthetic solid-state chemistry approach.
abundant heme molecule. Already in 1938, Cook described the activity of iron phthalocyanine (FePc), a synthetic analog of heme, toward the catalytic decomposition of H_2O_2 and later in the 1960s, Jasinski was able to show that different metal phthalocyanines were able to electrochemically catalyze the ORR in a fuel cell cathode.[17,18] A famous biomolecule that has the isostructural porphyrin motif of heme is chlorophyll, with the difference that the central metal ion, in this case, is Mg_2+. Coordination of Mg_2+ leads to the color shift from red to green, ultimately allowing for efficient light harvesting in photosynthesis.[19] In this regard, the aforementioned potential for Mg_2+ to direct the formation of MgN_4 does not come with a surprise.

Interestingly, modifications of both, heme and FePc, with Fe_2+ being substituted by Zn_2+ also exist, which suggests the possibility of realizing ZnN_4 sites embedded into carbon supports, which is isostructural to FeN_4 in Fe–N–Cs. An example of these modifications is found in case of iron deficiency or for people suffering from the “erythropoietic protoporphyria” disease, where throughout biosynthesis, the Fe_2+ is inefficiently incorporated into protoporphyrin, the precursor to the heme molecule.[20] Instead of heme, some Zn_2+-coordinated protoporphyrins are formed (Scheme 1C). Furthermore, zinc phthalocyanine (ZnPc) is a commercially available product used as catalyst, photosensitizer, etc.

After the success of our previous work based on Mg and the proof-of-principle for the general method of active-site imprinting, there are two reasons to move on with Zn-based carbons: 1) unlike for Mg, many literature studies are available on the preparation of porous carbon materials in the presence of Zn (especially involving ZnCl_2). This includes our own efforts e.g. reference 30, 34 and 40 in context with the Antonietti group et al. 2) The non-PGM/Fe–N–C community has recently increased involving Zn_2+-containing zeolitic imidazolium framework (ZIF)-based carbons with very interesting results.[21] It has to be mentioned that a few recent publications also reported on atomically dispersed Zn–N–C catalysts, which seems to be an upcoming topic.[22–24] Moreover, there are other potential advantages of using Zn, as further discussed.

Suitable mass-transport porosity is very important for the performance of catalysts in general, and especially for ORR electrocatalysts, which require the formation of three-phase boundaries. Often, advantageous morphologies are obtained with the hard template strategy, where an inorganic template acts as scaffold for the replication of the mesostructured morphology and removed after pyrolysis.[25–28] On the other hand, the drawback of this method is that corrosive chemicals are needed in order to remove the template, whereas hydrothermal and salt template/ionothermal syntheses have the advantages of avoiding this potential hazard.[29,30] In this regard, the selection of established synthetic methods involving zinc, leading to numerous NDCs with many different pore systems, is advantageous. Porous carbon preparation procedures involving Mg ions, in contrast, are rather rare.[31–33] Like for ZIF-8-derived carbons, for ZnCl_2-derived NDCs, relatively high residual amounts of Zn are reported, depending of course, on the synthesis temperature.[21,34] A partial removal of these residual amounts is possible by washing with concentrated acids, which points to strong coordination of Zn_2+ to the NDC support as in the case of complexes with chelating ligands.[34]

Herein, we report an adapted ionothermal carbonization recipe that targets the maximization of intermediate formation of macrocyclic ZnN_4 sites throughout carbonization, with the assumption that this will result in a high concentration of imprinted N_4 and ZnN_4 sites in the final porous Zn–N–C (Scheme 1D). The coordinated Zn_2+ ions within the obtained Zn–N–Cs are selectively exchanged with Fe_2+ or Fe_3+ to gain further understanding of the general properties of Fe–N–Cs and preferable preparation strategies. Fe–N–C catalysts with high Fe contents are prepared and investigated regarding their general structure as well as their ORR activity. The active site formation mechanism is further investigated using modern cutting-edge techniques. Identical location aberration-corrected scanning transmission electron microscopy (IL-ARSTEM) is used for the investigation of identical Fe–N–C voxels before and after the exchange of Zn_2+ with Fe_3+. The ion-exchange event is further studied using an in situ electrochemical flow cell (IEFC) coupled to an inductively coupled plasma mass spectrometer (ICP-MS).

2. Results and Discussion

2.1. Imprinting NDCs by Zn_2+ Templating (Zn–N–C)

The ionothermal carbonization involves 1,2-dicyanobenzene (phthalonitrile) as a carbon and nitrogen precursor (Scheme 1E). This compound is the precursor that is used for the organic synthesis of phthalocyanine macrocycles,[35] and an isomer of the precursor used in the original work on soft ionothermal carbonization at 600 °C by Kuhn et al.[36] Different LiCl–ZnCl_2 salt mixtures are used as combined solvent, porogen, and imprinting agent. The reaction mixture is prepared under dry conditions and then carbonized in Ar atmosphere. For convenience, samples are named XLi_Y(M), where X represents the molar ratio of LiCl in the salt mixture, Y stands for the carbonization temperature, and M represents Zn_2+ or Fe_2+/3+, indicating the coordinated metal ions.

Carbon materials with very high surface areas were obtained after aqueous acidic work-up in order to remove the salt and relatively loosely bound, i.e., physisorbed and probably N-coordinated or N–C-coordinated Zn_2+ with very high carbon yields in the range of ≈60%. Nitrogen sorption porosimetry was used to investigate the pore structure of the Zn–N–Cs. For all samples, a large nitrogen uptake at low relative pressure due to the presence of microporosity is observed (Figure S1, Supporting Information). In agreement with previous studies on ionothermal carbonizations, the porosity of XLi_Y can be controlled by changing solvent properties via the LiCl amount in the salt mixture, and an increase in mesoporosity is herein observed with increasing LiCl fractions (Figure S1 and Table S1, Supporting Information).[30,37] This leads also to tuned surface area, with samples synthesized with lower LiCl amount showing higher surface area, as high as 2069 m^2 g^-1. The temperature of carbonization only moderately influences the final porosity, with increasing temperatures (between 800 and 1000 °C) leading to slightly increasing abundance of pores smaller than ≈26 nm in diameter at the costs of the abundance of larger pores (26–50 nm); the surface area is also very similar.
in the range of 1430–1475 m² g⁻¹ (Figure S2 and Table S1, Supporting Information). Scanning electron microscopy (SEM) was used to investigate the morphology on the meso- and macroscale (pores larger than 50 nm), which is inaccessible to N₂ sorption porosimetry (Figure 1A). The optimized Zn–N–C sample 60Li₈₀₀(Zn²⁺) shows a hierarchical pore system, considered advantageous for mass transport, with an aerogel-type structure. Scanning transmission electron microscopy (STEM) imaging reveals an amorphous carbon structure with quasi-spherical mesopores, apparently originating from molten salt droplets acting as templates throughout synthesis as well as high amount of atomically dispersed metal atoms (Figure 1B; Figure S3, Supporting Information). Energy-dispersive X-ray spectra (EDX) show the presence of C, N, Zn, O, and Cl according to the precursor composition and pointing to relatively high amounts of strongly coordinated Zn²⁺ (Figure 1C). No crystalline inorganic phases were detected by powder X-ray diffractionometry (PXRD) with the spectrum showing the characteristic pattern for highly disordered carbons and no crystalline phase is detected. E) XPS of N 1s (left) and Zn 2p (right) with experimental data (black line) and peak fitting (dashed colored lines).

Figure 1. Morphological and chemical characterization of 60Li₈₀₀(Zn²⁺) with different techniques. A) SEM image shows the morphology on the meso- and macroscale. B) ADF STEM image shows atomically dispersed metal atoms. C) STEM–EDX spectrum shows the presence of C, N, Zn, O, and Cl; Au signal arises from the TEM grid. D) PXRD spectrum shows the characteristic pattern for highly disordered carbons and no crystalline phase is detected. E) XPS of N 1s (left) and Zn 2p (right) with experimental data (black line) and peak fitting (dashed colored lines).
near-edge X-ray absorption fine structure (NEXAFS). Figure S5 (Supporting Information) shows a comparison between these samples and two references, namely ZnO and ZnPc. Looking at the peak positions and at the shape of the Zn L₂,₃ edge, it can be stated that no ZnO phase is present and the coordination of Zn in the Zn–N–C materials well resembles the one in ZnPc. Moreover, since no clear difference is present, the composition of the sites seems not to significantly change between 700 and 1000 °C, confirming the XPS results. At this stage, since all the techniques employed strongly point in that direction, the formation of imprinted ZnN₄ sites seems reasonable.

60Li₈₀₀(Zn²⁺) was then separately subjected to Fe³⁺ coordination and Fe²⁺ coordination, respectively. Fe²⁺ was coordinated to 60Li₈₀₀(Zn²⁺) according to our previous procedure, with the difference of using higher Fe²⁺ concentrations. Fe³⁺ was coordinated using a novel molten salt approach. The coordination was carried out in a FeCl₃/LiCl mixture at 170 °C (T_m = 150 °C). The advantage of choosing a molten iron salt is that the depletion of Fe³⁺ ions throughout infiltration and coordination of the porous material can be nearly excluded, so each pore should be reached with Fe species. Fe³⁺ ions are also smaller compared to Fe²⁺ ions, possibly leading to the occupation of smaller coordination sites resulting in a higher concentration of N₄ sites. After washing again with diluted HCl in order to remove the remaining salt and loosely bound Fe ions, the samples were collected by filtration, dried at 80 °C overnight, and analyzed for coordination-induced changes.

2.2. Fe Coordination to Imprinted NDC (Fe–N–C)

Nitrogen sorption analysis after Fe coordination typically results in no qualitative changes in porosity, i.e., isotherms and pore size distributions remain qualitatively the same. This observation indicates that the carbon scaffold stays unchanged. However, reduced quantitative values resulting from a downshift of the isotherms are observed, pointing to an increased specific weight of the sample after transmetalation employing the FeCl₃/LiCl mixture. The coordination with FeCl₃ in MeOH, on the other side, leads to an upshift of the isotherm, pointing to a decrease in the specific weight of the sample. This difference is also reflected in the elemental analysis of the two samples, with 60Li₈₀₀(Fe³⁺) having Fe and Zn amounts of 3.12 and 0.56 wt% and 60Li₈₀₀(Fe²⁺) of 0.55 and 2.27 wt%, respectively, after correction for the water content (Table S2, Supporting Information). The ICP-MS results show a decrease in Zn content, very pronounced especially in the case of 60Li₈₀₀(Fe³⁺), suggesting the replacement of Zn²⁺ by Fe ions. 60Li₈₀₀(Fe²⁺) and 60Li₈₀₀(Fe³⁺) show specific surface areas (SSAs) of 1707 and 1147 m² g⁻¹, and total pore volumes (TPVs) of 2.43 and 1.07 cm³ g⁻¹, respectively (Table S1, Supporting Information). SEM and STEM imaging after Fe coordination reveal no apparent changes in the carbon morphology due to Fe coordination, suggesting the successful coordination of atomically dispersed Fe only (Figure 2A,B; Figure S6, Supporting Information). STEM–EDX analysis clearly proves the presence of Fe, confirming the

Figure 2. Morphological and chemical characterization of 60Li₈₀₀(Fe³⁺) with different techniques. A) SEM image does not show any change on the meso- and macroscale due to transmetalation. B) ADF STEM image shows higher density of atomically dispersed metal atoms. C) STEM–EDX spectrum shows the same composition of the sample before transmetalation with the addition of Fe peaks; Au signal arises from the TEM grid. D) PXRD spectrum shows the characteristic pattern for highly disordered carbons and no crystalline phase is detected, as for the sample before transmetalation. E) XPS of N 1s (left) and Zn 2p (right) with experimental data (black line) and peak fitting (dashed colored lines).
successful introduction of Fe in an atomically dispersed form (Figure 2C). PXRD additionally confirms the absence of crystalline inorganic phases, as expected after the acidic work-up, which followed the coordination step (Figure 2D). XPS survey show residual amounts of zinc (2.25 wt% Zn for 60Li$_800$(Fe$_2^{2+}$) and 0.39 wt% Zn for 60Li$_800$(Fe$_3^{3+}$)) and allow for the quantification of the iron content to 0.57 wt% Fe for 60Li$_800$(Fe$_2^{2+}$) and 0.54 wt% Fe for 60Li$_800$(Fe$_3^{3+}$) (Figure 2E; Figure S7, Supporting Information). Since all other techniques employed point to much higher concentrations of atomically dispersed Fe, XPS analysis is likely underestimating the concentrations due to its surface sensitivity.

For the investigation of the nature of the obtained Fe complexes (degree of covalent bonding, spin state, etc.), the Fe$_2^{2+}$ and Fe$_3^{3+}$ coordinated samples 60Li$_800$(Fe$_2^{2+}$) and 60Li$_800$(Fe$_3^{3+}$) were independently investigated by Mössbauer spectroscopy. In this context, it is worth mentioning that with the pyrolytic state-of-the-art preparation of Fe–N–Cs, a deliberate selection of the oxidation state of Fe is not possible due to carbothermal reduction. Pyrolysisis-derived Fe–N–Cs seem to be mostly consisting of Fe$_2^{2+}$ species and, therefore, Fe$_3^{3+}$ species are often not considered for the interpretation of the spectra.[41] A sextet, originating from super-paramagnetically coupled species, is however assigned to Fe$_2^{2+}$ species and its $d^5$ electron configuration. We recorded Mössbauer spectra of 60Li$_800$(Fe$_3^{3+}$) and 60Li$_800$(Fe$_2^{2+}$) at room temperature (RT) and 4.2 K, respectively (Figure 3).

Looking at the room-temperature spectra, it can be stated that no sextets or singlets are observed. Accordingly, no non-nanometric iron side phases (i.e., metallic iron or iron carbide) that would be super-paramagnetic at room temperature are present after the acidic work-up. This is in contrast to many pyrolytic Fe–N–C syntheses, in which particles of such phases may be covered by graphitic shells and therefore protected from acidic removal.[9] Liquid helium temperature measurements were performed to distinguish between the desired active FeN$_4$ sites and nanoscopic iron species, which exhibit quadrupole doublets at RT either because they are not magnetically ordered or super-paramagnetic but exhibit a magnetic hyperfine splitting at 4.2 K, where their super-paramagnetism is blocked.[42]

At 4.2 K, indeed, what we called D2 disappears and apparently splits into a sextet (two for 60Li$_800$(Fe$_2^{2+}$)). At this temperature, although, two doublets (named D1 and D3) give still a strong signal, namely 37.1% and 5.7% of the total spectrum for 60Li$_800$(Fe$_3^{3+}$) and 39.2% and 9.9% for 60Li$_800$(Fe$_2^{2+}$). Surprisingly, regardless of the transmetalation procedure (Fe$_2^{2+}$ vs Fe$_3^{3+}$), these two samples have very similar Mössbauer spectra. As already indicated by ICP-MS measurements, 60Li$_800$(Fe$_3^{3+}$) shows ≈4 times higher Fe content compared to 60Li$_800$(Fe$_2^{2+}$) (Table S2, Supporting Information), pointing to the effectiveness of the novel molten salt approach used for the transmetalation, especially since the resulting structure...
of Fe sites is apparently equal. Compared to conventional Fe–N–C–Cs, it is interesting to observe the large abundance of the magnetically coupled Fe\textsuperscript{iii} species in the 4.2 K spectra. This is notable since the coordination with Fe\textsuperscript{ii} also leads to the large abundance of magnetic Fe\textsuperscript{ii} ions. This observation may be explained by both the contact to oxygen in the ambient atmosphere and the treatment with the oxidative acid. The larger extent of oxidation of Fe\textsuperscript{ii} to Fe\textsuperscript{iii} species compared to conventional Fe–N–C is not surprising because here the entire number of complexes is surface complexes, and therefore fully accessible to oxygen of the atmosphere. Even more intriguing is, however, the fact that these species resist the acid work-up. The Mössbauer parameters for each component are given in Table S3 (Supporting Information). The two quadrupole doublets that remain at 4.2 K are well known in the Fe–N–C community and are typically assigned to different spin configurations of the Fe\textsubscript{N\textsubscript{3}} sites.\textsuperscript{[43]} D1 can be assigned to strongly covalent Fe\textsuperscript{ii} as in Fe porphyrin. According to its Mössbauer parameters, it can, however, also be assigned to Fe\textsuperscript{ii}. Comparison of samples 60Li\textsubscript{800}(Fe\textsuperscript{iii}) and 60Li\textsubscript{800}(Fe\textsuperscript{ii}) reveals very similar parameters for the D1 doublets, suggesting the possibility that regardless of the initial oxidation state of the iron, the same species are formed. D3 can certainly be assigned to high-spin Fe\textsuperscript{iii}, perhaps with a moderately covalent character. Considering that for 60Li\textsubscript{800}(Fe\textsuperscript{ii}) no Fe\textsuperscript{ii} would be expected, this result is somewhat surprising and requires further investigation. The sextet in the 4.2 K spectra is assigned to nanometric oxidic clusters, in which the Fe atoms are close to each other in a magnetically ordered arrangement; such clusters are also visible in the transmission electron microscopy (TEM) picture of 60Li\textsubscript{800}(Fe\textsuperscript{iii}) (Figure S8, Supporting Information). The high abundance of such species may be explained by the high abundance of micropores in the original NDC scaffold.

In order to further elucidate these data, additional samples were analyzed. 60Li\textsubscript{800}(Zn–Fe) was prepared in the same fashion as 60Li\textsubscript{800}(Zn\textsuperscript{ii}) but containing 2.2 wt\% Fe of FeCl\textsubscript{3} (with respect to the precursor) in the mixture prior to heat treatment, resembling the classic route to synthesize Fe–N–C catalysts.\textsuperscript{[44]} The aforementioned sample was further subject to transmetalation with the novel ionothermal approach, leading to the catalyst 60Li\textsubscript{800}(Fe–Fe\textsuperscript{ii}). Due to the low Fe content, the Mössbauer spectrum of 60Li\textsubscript{800}(Zn–Fe) is too noisy to draw any conclusion. On the other hand, 60Li\textsubscript{800}(Fe–Fe\textsuperscript{iii}) shows a clear spectrum, very similar compared to 60Li\textsubscript{800}(Fe\textsuperscript{ii}) and 60Li\textsubscript{800}(Fe\textsuperscript{iii}) both at room temperature and 4.2 K (Figure S9, Supporting Information).

After this comparison, it is possible to draw the following conclusions: 1) the novel molten salt approach using a FeCl\textsubscript{3}/LiCl mixture is capable of loading more Fe onto the samples compared to the wet-chemical coordination step using FeCl\textsubscript{3} in MeOH. 2) The final configuration of Fe in the catalyst seems not to depend on the Fe source used during the transmetalation, but rather can be determined by the fact that the active sites have been imprinted by Zn\textsuperscript{ii}. 3) It seems that once the Fe ions fill all the available pockets, they start to form some magnetic ordered structure. This indicates the possibility that Mössbauer spectroscopy could be used to track the status of the transmetalation process.

The electrocatalytic activity toward the ORR was tested in the PEMFC-relevant acidic conditions using a standard three-electrode rotating (ring) disk electrode (R|RDE) setup with O\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} as the electrolyte and a freshly calibrated and separated RHE reference electrode. Comparison of the activities at 1600 rpm of the equally loaded samples (290 µg cm\textsuperscript{-2} without taking into consideration the water content), 60Li\textsubscript{800}(Zn\textsuperscript{ii}), 60Li\textsubscript{800}(Fe\textsuperscript{ii}), and 60Li\textsubscript{800}(Fe\textsuperscript{iii}), shows a strong positive shift of ≈323 mV for 60Li\textsubscript{800}(Fe\textsuperscript{ii}) and ≈383 mV for 60Li\textsubscript{800}(Fe\textsuperscript{iii}) toward higher ORR activity compared to 60Li\textsubscript{800}(Zn\textsuperscript{ii}) (Figure 4A). The onsets of the electrocatalytic reaction are found at relatively low overpotentials at ≈0.85 V for 60Li\textsubscript{800}(Fe\textsuperscript{iii}). The moderate slopes in the mixed kinetic diffusion-controlled regime, related to Tafel slopes of ≈108 mV dec\textsuperscript{-1} for 60Li\textsubscript{800}(Fe\textsuperscript{ii}) and ≈83 mV dec\textsuperscript{-1} for 60Li\textsubscript{800}(Fe\textsuperscript{iii}), lead to a moderate half-wave potential \textit{E}_{1/2} of 0.66 V for 60Li\textsubscript{800}(Fe\textsuperscript{ii}) and a more promising \textit{E}_{1/2} of 0.72 V for 60Li\textsubscript{800}(Fe\textsuperscript{iii}). An increase in the loading could herein be utilized to shift the \textit{E}_{1/2} values positively, but considering the high Fe concentrations and the high amount of micropores, in which active sites are supposed to be hosted,\textsuperscript{[45–47]} even more positive values would be expected. Based on our previous study on ionothermal carbons as ORR catalysts in alkaline electrolyte, we assign the relatively low slopes to a limited catalyst utilization originating from high abundance of so-called bottleneck pores. Further optimization of the nanopore systems seems reasonable, but is beyond the scope of the present work. The limiting current of both catalysts approaches the theoretical limiting current density of 5.6 mA cm\textsuperscript{-2} at 1600 rpm pointing at a complete reduction of O\textsubscript{2} to H\textsubscript{2}O in a four-electron reduction at this catalyst loading. Comparing the same loading of 290 µg cm\textsuperscript{-2} for both catalysts, RRDE measurements reveal a more selective reduction of O\textsubscript{2} for 60Li\textsubscript{800}(Fe\textsuperscript{iii}) with a maximum peroxide yield of 7% at ≈0.55 V compared to 17% for 60Li\textsubscript{800}(Fe\textsuperscript{ii}) (Figure S10, Supporting Information). Routécky–Levich analysis reveals a kinetic current density \textit{j}_{\text{KLP}} of 15.5 mA cm\textsuperscript{-2} (at 0.6 V) for 60Li\textsubscript{800}(Fe\textsuperscript{ii}) and 10.4 mA cm\textsuperscript{-2} (at 0.7 V) for 60Li\textsubscript{800}(Fe\textsuperscript{iii}), respectively (Figure S11, Supporting Information).

For Fe–N–C catalysts the main degradation mechanisms that are usually discussed are iron-ion dissolution, electrochemical carbon corrosion, protonation of N-groups, and surface oxidation induced by H\textsubscript{2}O\textsubscript{2}. To investigate the degradation of our catalysts in this regard, we carried out an accelerated stress test over the most active catalyst 60Li\textsubscript{800}(Fe\textsuperscript{iii}), using voltammetric cycling (between 0.4 and 0.8 V for up to 500 cycles at a scan rate of 50 mV s\textsuperscript{-1}) in both O\textsubscript{2}- and Ar-saturated electrolytes (Figure 4A and Figure 4B, respectively). Interestingly, there is no degradation (quantified by the shift of the half-wave potential) observed in the Ar case, whereas in O\textsubscript{2}-saturated electrolyte, we observed a high degradation rate in the first few hundred cycles, eventually leveling out toward the 500th cycle. The reduction of the half-wave potential after 500 cycles amounts to ≈45 mV, indicating relatively high sensitivity toward oxidation. Recent literatures suggest the role of peroxide species in reducing the activity of Fe–N–C catalysts throughout operation.\textsuperscript{[48,49]} Our results confirm these reports and suggest that additional active sites/materials catalyzing the disproportionation of peroxide species might be important for the mitigation of the oxidation in future catalysts.
The activity of the sample obtained from the pyrolysis experiment with the addition of FeCl$_3$ in the ZnCl$_2$/LiCl mixture, namely 60Li$_{800}$(Zn–Fe), and the activity of the same sample after transmetalation, 60Li$_{800}$(Fe–Fe$^{3+}$), already presented in the Mössbauer part, have also been investigated. Figure S12 (Supporting Information) shows an exemplary comparison of the Mössbauer part, have also been investigated. Figure S12 (Supporting Information) shows an exemplary comparison between these two samples and 60Li$_{800}$(Fe$^{3+}$).

At this comparison, two facts are worth mentioning: 1) our novel approach based on active-site imprinting followed by metatransmetalation is capable of producing catalysts with the same activity as in the case of pyrolytic synthesis, but with the chance of surpassing the limitation due to metastability of the FeN$_4$ sites at high temperatures; 2) 60Li$_{800}$(Fe–Fe$^{3+}$) does not show any improvement compared to 60Li$_{800}$(Zn–Fe), meaning that the added iron is not contributing to the activity, either because it is forming small oxidic clusters [see Mössbauer part] or because it is occupying N$_x$ sites, which are not active toward the ORR. Although intriguing, unveiling this observation is beyond the scope of this manuscript, and more detailed characterizations will be performed in the future.

However, when comparing 60Li$_{800}$(Zn$^{2+}$), 60Li$_{800}$(Fe$^{2+}$), and 60Li$_{800}$(Fe$^{3+}$), it cannot be disregarded that the positive shift of the ORR is extraordinarily large, which is very important considering the mild procedure of the active-site formation. The results imply a very large potential of the imprinting metallation method for the rational design of future M–N–C catalysts. In the concluding part of this work, the focus will be on the fundamental question of the formation mechanism of the FeN$_4$ sites at low temperature.

### 2.3. Mechanistic Study

Although the increase in activity is remarkable, this remains only an indirect proof for the transmetalation of imprinted active sites. In order to unambiguously demonstrate this process, 60Li$_{800}$(Zn$^{2+}$) was placed on a gold grid for identical location TEM (IL-TEM), and the transmetalation was carried out using a solution of FeCl$_2$ in 0.1 M HClO$_4$, sequentially washing with fresh 0.1 M HClO$_4$. Figure S5 shows annular-dark-field (ADF) STEM images of the same area of a carbon particle before (upper row) and after (middle row) transmetalation with the respective EDX spectra. Before transmetalation, only atomically dispersed Zn atoms are present and no Fe is detected. On the other hand, after transmetalation, the density of atomically dispersed metal atoms is clearly higher with the EDX spectrum showing the presence of Fe.

Lately, many interesting techniques have been adopted to characterize Fe–N–C catalysts. Besides IL-TEM, ICP-MS coupled to an EFC system has proved to be a powerful tool. In this study, we applied the aforementioned technique to follow the transmetalation in situ. The main idea was to record the activity of 60Li$_{800}$(Zn$^{2+}$), while exchanging Zn with Fe. However, the EFC setup is not optimized for recording ORR activity, and the obtained values cannot be directly compared to the ones obtained with an RDE setup due to different hydrodynamics: moreover, the Fe content in the carrying solution had to be low due to limitations related to the saturation of the signal in the MS; for these reasons, it was not possible to observe a shift in the activity as big as in the RDE when comparing 60Li$_{800}$(Zn$^{2+}$) with 60Li$_{800}$(Fe$^{2+}$). At this point, we decided to use the EFC–ICP-MS in a different fashion.

To confirm complexation of Fe atoms, 60Li$_{800}$(Zn$^{2+}$) was cycled between −0.5 and 1.6 V after flowing an ≈10 ppb solution of FeCl$_2$ in 0.1 M HClO$_4$ on the sample. It has already been reported that at high potentials the oxidation of the carbon material directly leads to destruction of the carbon surface with a consequent release of the components of the just formed active sites. For comparison, the same set of experiments, including complexation and degradation, has been carried out on an NDC reproduced from the literature. In this material, no imprinting metal is present and hence no N$_x$-type anchoring
sites for Fe are to be expected. Although the coordination of Fe to terminal N sites cannot be excluded, for this material, loosely bound Fe species that are considered less active and stable are the most likely case.

The MS spectra for the two samples are shown in Figure 5 (lower row). For 60Li_800(Zn²⁺), as expected, several Fe (as well as Zn) peaks are observed during cycling, confirming that the transmetalation (or metalation) has taken place, whereas, for the NDC with a random distribution of N atoms, no peaks are observed.

In conclusion, we reported a new synthetic route for Fe–N–C catalysts starting from Zn–N–C materials in which Zn²⁺ ions act as active-site imprinter, followed by low-temperature Fe coordination. The Zn–N–Cs possess very high surface area and tuned properties obtained by simply using a LiCl–ZnCl₂ salt mixture as the reaction medium; also, the high yields and the easiness of sample processing make this synthesis promising for large-scale production. We showed that a novel molten salt transmetalation approach is capable of loading more Fe compared to our previously reported method involving FeCl₂ in MeOH. Besides, we demonstrated that Fe coordination is independent of the Fe source employed for the transmetalation event (Fe²⁺ vs Fe³⁺).

In addition to the indirect proof of the activity gain in RDE, we visualized the transmetalation process with cutting-edge techniques such as IL-TEM and EFC–ICP-MS.

This work further proves the effectiveness of our active-site imprinting strategy already reported using Mg²⁺ as an active-site imprinter, which makes it possible to decouple the formation of the carbon scaffold from the one of the active site,
possibly surpassing the limitation of current synthetic methods, which rely on kinetic stabilization of Fe atoms at high temperatures. Also, the use of different imprinting metals could lead to different Fe configurations with enhanced activity, something that is not straightforward with current synthesis procedures.

We believe that our work will open new frontiers in both the synthesis and the understanding of Fe–N–C catalysts and M–N–C materials in general.

3. Experimental Section

Materials and Methods: 1,2-dicyanobenzene, LiCl, ZnCl₂, FeCl₂, FeCl₃, and methanol were purchased from Sigma Aldrich. All chemicals were used without further purification.

In a typical synthesis, 1,2-dicyanobenzene (0.7 g) was thoroughly mixed with the respective LiCl–ZnCl₂ mixture (7 g) prior to the heat treatment. The resulting mixtures were placed in an alumina crucible covered with a quartz lid and heated to the desired temperature with a heating rate of 10 K min⁻¹ in a tube furnace. After holding the temperature for 1 h, the samples were let in the tube to cool down to room temperature. All steps were conducted with a constant Ar flow. The obtained materials were ground and washed with 0.1 M HCl for several hours. Finally, the samples were dried at 80 °C overnight.

Coordination of iron was carried out in two different fashions. 60Li₁₋₇Fe₀ (Fe⁺³) was prepared from 60Li₁₋₇Zn₀ (Zn⁺²) employing the metal-coordination procedure from ref. [16]. 60Li₁₋₇Fe₀ (Fe⁺³) was obtained after mixing ~0.1 g of 60Li₁₋₇Zn₀ (Zn⁺²) with ~3 g of LiCl–FeCl₃ eutectic mixture in a Schlenk tube, heating up to 170 °C for 22 h in Ar atmosphere, and washing with 0.1 M HCl for several hours and drying.

Characterization: N₂ sorption measurements were carried out using Quantachrome Autosorb iQ2. The samples were outgassed at 250 °C under vacuum overnight prior to the measurements. The data were collected between 10⁻³ and 1 P/P₀. Specific surface areas were determined according to Brunauer–Emmett–Teller (BET) theory using Micropore BET Assistant supplied by Quantachrome ASIQwin software. The total pore volume was calculated at P/P₀ = 0.99 using Quantachrome Autosorb iQ2. The pore size distributions were calculated with the quenched-solid density functional theory (QSDFT) method ( slit/cylindrical/spherical pores). For the morphological examinations, the samples were characterized using a field-emission FE-SEM Zeiss Ultra Plus microscope.

STEM imaging was performed with a beam current of ~1.45 pA and an accelerating voltage of 80 kV in an atomic resolution aberration-corrected scanning transmission electron microscope ARM 200CF. Sample preparation was carried out by diluting the sample powder in ethanol and drop-casting the solution on lacey carbon support Au grids.

XRD data were recorded with a StadiP diffraactometer with Cu Kα radiation (λ = 1.54060, 50 kV, 30 mA, germanium (111)).

XPS measurements were conducted using a Kratos Axis Supra spectrometer with monochromatized Al Kα radiation. Samples were prepared by dispersing the powder in an isopropanol and water mixture followed by drop-casting on Cu tape. Each spectrum was acquired with 0.1 eV step size and corrected with respect to C 1s peak at 284.7 eV. Data analysis was performed with ESCAA software.

NEXAFS spectra were collected at the soft X-ray analytics facility WERA of the Institut für Festkörperphysik at the Karlsruhe Synchrotron ANKA, Germany. Partial fluorescence-yield detection was used. The photon energy was calibrated to better than 30 meV by simultaneously measuring a NIO reference sample at the Ni L₂ edge.

Mössbauer spectra were recorded with a sinusoidal velocity waveform at room temperature and at 4.2 K on powder samples enclosed in lucite holders. For the low-temperature measurements, both the absorber and the ⁵⁷Co in rhodium source were cooled in a liquid helium bath cryostat. MOS90 software (version 2.2) was used for the fitting of the spectra. Isomer shifts were measured with respect to the source having the same temperature as the absorber. In order to refer the shifts to α-Fe at room temperature, 0.115 mm s⁻¹ was added to the shifts measured at room temperature and 0.245 mm s⁻¹ to those measured at 4.2 K.

The coupling of EFC with ICP-MS was already introduced in previous publications[52,53] Briefly, a replica of BASi electrochemical flow cell (Cross-Flow Cell Kit MW-5052) made of polytetrafluorethylene (PEEK) was coupled with an Agilent quadrupole ICP-MS instrument (Agilent 7900, Agilent Technologies, Santa Clara, CA), equipped with MicroMist glass concentric nebulizer and Peltier-cooled, Scott type spray chamber. Upstream the EFC, a diagonal four-way flow valve (idex, V-1000D, from PEEK) was used to switch from 0.1 M HClO₄ (Merck, Suprapur) and the 10 ppb FeCl₃ in HClO₄ solution. Two syringe pumps (WPI sp100i and Harvard apparatus 11 plus) were used to pump the appropriate solution at a constant flow of 400 μL min⁻¹. The working and counter electrodes were made of glassy carbon, while the reference electrode was a Ag/AgCl electrode (BASi). The potential of the reference related to RHE was determined prior to flow experiments in a separate cell versus a Pt electrode in 0.1 M HClO₄ saturated with H₂. The orientation of the working electrode and the counter electrode was adjusted, so the inlet of the electrolyte flow was at the counter electrode and the outlet was at the working electrode to avoid any redeposition. Electrochemical control was established with a potentiostat (CompactStat.e, Ivium technology). The catalyst thin films were prepared by drop-casting 5 μL of a 1 mg mL⁻¹ well-dispersed suspension of the catalyst. After evaporation of the solvent, 2 μL of a 9 mg mL⁻¹ Teflon suspension was drop-cast on the catalyst layer. Zn and Fe amounts in the synthesized materials were quantified by the same ICP-MS.

Electrochemical measurements were carried out in a three-electrode glass cell using Ar- and O₂-saturated 0.1 M HClO₄ prepared from a 60% solution (Guaranteed Reagent, Kanto Chemical) and deionized ultrapure water (Milli-Q Integral 5, 18.2 MΩ cm). An Autolab PGSTAT302N (Metrohm) potentiostat was employed for the measurements. A freshly prepared RHE was used as the reference electrode and an Au wire as the counter electrode. The solution resistance was determined by electrochemical impedance spectroscopy and the reported potentials (except for those of the accelerated stress tests) were corrected accordingly. The reported polarization curves for ORR were corrected for capacitive currents by subtracting the curves recorded in Ar-saturated electrolyte from the ones recorded in O₂-saturated electrolyte. The catalyst inks were prepared by dispersing 5 mg of catalyst powder in 840 μL of N,N-dimethylformamide (≥99.8, Fisher Scientific), followed by sonication for 30 min. Afterward, an aliquot of 50 μL of 5 wt% Nafion suspension (Sigma-Aldrich) was added and the ink was sonicated for 10 min more. Subsequently, 10 μL of ink was drop-cast onto a well-polished glassy carbon electrode (Ø = 5 mm, obtained from Pine Research Instrumentation) and dried under an infrared heater for 60 min. The resulting catalyst loading was 290 μg cm⁻². The accelerated stress tests were conducted by cycling between 0.4 and 0.8 V at 400 rpm and with a scan rate of 50 mV s⁻¹.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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