

# On the effect of sulfite ions on the structural composition and ORR activity of Fe-N-C catalysts

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Abstract Fe-N-C catalysts are the most promising group of non-precious metal catalysts for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFC). This study focusses on two different porphyrin-based Fe-N-C catalysts and a Fe-N-C catalyst prepared from alternative precursors under S-addition. Catalysts are subjected to a wet-chemical poisoning treatment by sulfite ions (SO<sub>3</sub><sup>2-</sup>). A mechanism for the deactivation process of the active sites is proposed. ORR activity is evaluated for the original catalysts (OC) and for the poisoned catalysts in 0.1 M H<sub>2</sub>SO<sub>4</sub>. In addition, the structural composition of the catalysts is identified by Mößbauer spectroscopy. Our results show that the sulfite ions bound irreversible to the catalysts and the catalysts lose significant fractions of their ORR activity while in Mößbauer spectroscopy a new doublet appears. Based on the results, possible models for the binding of the ambident sulfite ion to the FeN<sub>4</sub> centers are discussed.

Keywords Fe-N-C catalyst  $\cdot$  Mößbauer spectroscopy  $\cdot$  PEMFC  $\cdot$  oxygen reduction reaction

This article is part of the Topical Collection on Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2017), Saint-Petersburg, Russia, 3-8 September 2017 Edited by Valentin Semenov

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### **1** Introduction

State of the art proton exchange membrane fuel cells (PEMFC) make use of platinum-based catalysts (Pt/C). A major drawback for the use of Pt/C catalysts is the high cost which contributes by >25 % to the overall cost of the FC system. Fe-N-C catalysts are so far the most promising alternative for the oxygen reduction reaction (ORR) [1–3]. They are prepared from a heat-treatment of FeN<sub>4</sub> macrocycles or alternative iron, nitrogen and carbon precursors [1, 4, 5]. Further treatments as acid-leaching steps or additional heat-treatments in inert or reactive gas atmospheres are often added for the optimization of the catalysts [6–11]. Nevertheless, most of the catalysts have a heterogeneous composition involving inorganic iron species and FeN<sub>x</sub> sites. Own reports and others showed that the ORR activity can be assigned to a ferrous FeN<sub>4</sub> site with iron in the low-spin state [6, 12, 13]. Hence, due to the molecular structure of active sites, <sup>57</sup>Fe Mößbauer spectroscopy (MS) is the best suited technique for the structural characterization [6, 13, 14]. One mayor challenge is a fundamental understanding of the ORR active site, which is important to elucidate the oxygen reduction cycle on Fe-N-C catalysts and how these catalysts might get deactivated.

In recent reports it was shown that inducing the chemisorption of species on active sites can shine additional light on their electronic configuration [15, 16]. The strategy is well-known for platinum-based catalysts where e.g. CO is adsorbed on the surface and based on the charge assigned to the subsequent oxidation of CO the electrochemical active surface area of platinum is determined [17]. While for molecular FeN<sub>4</sub> macrocycles CO can be used as poison [18] a similar approach for Fe-N-C catalysts failed [19]. CO sorption is only possible at low temperatures but can then be used for determination of surface accessible active sites [20]. Just only recently, attempts to adsorb probe molecules on Fe-N-C catalysts in-situ were successful [15, 16]. The number of electrochemical active sites and structural changes were identified.

In a previous study performed at the Hahn-Meitner-Institute in Berlin (now Helmholtz-Center Berlin) it was investigated to what extend the presence of different species affects the ORR activity of Co-based Me-N-C catalysts [21]. The ORR activity was therefore measured in pure electrolyte and after addition of different quantities of poisons. A strong effect on ORR activity was found by the addition of sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>). It should be pointed out that the activity was evaluated in the presence of the poison-containing electrolyte. It was not investigated whether the poison remained chemisorbed by a change of the electrolyte or not. In addition, the study focused on the electrochemistry without any structural characterization.

In a previous study under the contribution by one of the authors, it was shown that specifically prepared Fe-N-C catalysts were prone to an irreversible and recoverable activity decay [22]. The irreversible decay is directly induced by putting the catalyst into contact with water or acidic electrolyte and attributed to the leaching of very weakly bonded sites that have some activity for the ORR. As such instable sites are not of technological relevance an acid leaching of the catalysts can help to omit the contribution assigned to immediate, irreversible activity losses.

More interesting is the recoverable activity decay. Herranz et al. showed that an additional loss of 8 % of the remaining activity is lost upon contact of the active sites with anions [22]. On the one hand, the anions were unambiguously identified by different techniques including X-ray induced photoelectron spectroscopy, thermogravimetry coupled with massspectroscopy and timeofflight secondary ion mass spectroscopy. On the other hand, it was difficult to identify the adsorption site for these anions, due to low quantity of ORR active sites and a heterogeneous composition of the catalyst. We will come back to this work, later. First, the expectation in terms of spectroscopic changes induced by the interaction of an anion with FeN<sub>4</sub> sites should be discussed.

In an early work by Taube it was shown that FeN<sub>4</sub> sites in iron phthalocyanine can bind anions from the corresponding acids in axial direction. Induced by the change in the local environment and charge distribution the Mößbauer parameters changed [23]. Indeed, for porphyrin-based Fe-N-C catalysts a long-term stability test in 0.5 M H<sub>2</sub>SO<sub>4</sub> let to the formation of an additional doublet in Mößbauer spectroscopy ( $\delta = 0.08 \text{ mm s}^{-1}, \Delta E_Q = 3.28 \text{ mm s}^{-1}$ ). The doublet was attributed to the interaction of FeN<sub>4</sub> sites with HSO<sub>4</sub> [24]. Hence, the works by Taube [23] and Kramm [24] confirm that an axial binding of anions to FeN<sub>4</sub> sites should be detectable by Mößbauer spectroscopy.

A similar approach by Mößbauer spectroscopy was also tried out in the publication by Herranz et al. [22]. Due to very small iron contents in the investigated catalysts (0.07 wt%) with only partial enrichment in Fe-57, Mößbauer spectra (as obtained after four weeks of measurement time) gave no significant difference for the poisoned and recovered catalyst. Based on this it was concluded that in this case, the anions do not bind directly to the FeN<sub>4</sub> centers. Instead it was suggested that they bind to protonated nitrogen atoms in the vicinity of active sites Such binary FeN<sub>4</sub>...NH<sup>+</sup> sites were found to reduce oxygen significantly faster. Recently, the acceleration of ORR on MeN<sub>4</sub> sites by protonated functional groups was confirmed by theoretical calculations [25].

Today, there are several different catalyst preparation approaches that enable preparation of highly purified catalysts and/or with relatively high concentrations of iron species [7, 13, 26]. This enables a more easy detection of structural changes, even though only a partial fraction of active sites might be blocked as indicated in the work from Malko and Kucernak [15].

Motivated by the significantly improved understanding of the active site in Fe-N-C catalyst during the last decade and all the recent findings, we adapted therefore the Na<sub>2</sub>SO<sub>3</sub> poisoning treatment reported by Knauer [21]. In contrast to his work, poisoning was performed ex-situ on catalyst powders in order to obtain sufficient catalyst masses to perform Mößbauer spectroscopy. ORR activity was measured on the original catalyst and after treatment with Na<sub>2</sub>SO<sub>3</sub>. The results indicate that indeed Na<sub>2</sub>SO<sub>3</sub> can be used as poison for the deactivation of Fe-N-C catalysts. Based on redox-chemistry, either SO<sub>3</sub><sup>2-</sup>, HSO<sub>3</sub> or SO<sub>4</sub> might be possible species to adsorb on molecular FeN<sub>4</sub> sites [27]. While the Mößbauer spectra showed the appearance of an additional species, the ORR activity is significantly lowered.

# 2 Experimental part

#### 2.1 Sample preparation

For the poison experiments three different Fe-N-C catalysts were prepared. As we focused on the deactivation behavior of the catalysts, the catalyst preparation will only be shortly described. More detailed description of the preparations can be found in Kramm et al. [12] and Janßen et al. [28].

Two catalysts were prepared from iron porphyrin (FeTMPPCl, TriPorTech) supported on carbon precursor, with 2.1 wt% Fe (95 % Fe-57) on Ketjen Black 600. The precursor was subjected to a heat-treatment in inert gas atmosphere with a heating ramp of 300 °C h<sup>-1</sup> to the desired end temperature were the sample was kept for 30 min. After cooling down the sample was transferred into 1 M HCl and acid leached overnight, whereas the suspension

was placed for 1 hour in an ultrasonic bath. After filtration and drying the catalysts were obtained as black powders. These samples are labeled as HT600HCl and HT800HCl in order to indicate that samples were prepared with a final heating temperature of 600 °C and 800 °C.

A third sample was prepared by slight modification of the procedure described in Janßen et al. [28]. The precursor mixture contained dicyandiamide, 1,10-phenanthroline, iron acetate and sulfur with S/Fe = 2.45. The oven program was different compared to the porphyrin-based catalysts due to significant larger mass losses during the heat-treatment. The sample was treated at 300 °C for 30 min then at 500 °C for 30 min und finally at 800 °C for 60 min (heating ramp 300 °C h<sup>-1</sup> in inert gas). Acid leaching was performed in 2 M HCl. In order to increase the activity, after filtration and drying the catalyst was subjected to a second heat-treatment for 30 min at 800 °C (heating ramp: 600 °C h<sup>-1</sup> in inert gas). The obtained catalyst is labeled as HT800HCl+S.

#### 2.2 Poisoning treatment

The poisoning effect was previously described by Knauer [21] for Co-N-C catalysts but adapted in this work. For each poisoning treatment 50 mg of the original catalyst were placed in 100 ml 0.1 M  $H_2SO_4$  with the addition of 5 mM  $Na_2SO_3$ . In order to enhance the interaction, the samples were placed in an (US bath) for 1 h. Afterwards the catalyst was filtered, washed with distilled water and dried overnight at 80 °C in an oven.

The original and poisoned catalysts were characterized by Mößbauer spectroscopy and electrochemically.

#### 2.3 Electrochemistry

RDE measurements were performed with an ECi-200 potentiostat from Nordic Electrochemistry combined with an "EDI101" Rotating Disk Electrode setup from Radiometer. A three electrode setup was used with an Ag/AgCl/ 3 M KCl reference electrode and a Glassy Carbon (GC) rod as counter electrode. The working electrode was a GC disk (0.1963 cm<sup>2</sup>). For the catalyst ink 5 mg catalyst powder were mixed with 223  $\mu$ l of a 1.1 wt% Nafion solution (N/C = 0.48).

Original catalysts were treated as usual: that means the suspension was placed for 15 min in an US bath, followed by dispersion with an ultrasonic finger and 5 min on a Vortexer. 5  $\mu$ l of this ink were placed on the GC disk and left for drying (catalyst loading: 0.57 mg cm<sup>-2</sup>). For the poisoned catalysts the ink recipe was the same but the suspension was only shaked manually to avoid a possible detachment of the poison from the catalyst [16]. The catalyst loading was the same.

The electrochemical measurements were started in O<sub>2</sub> saturated electrolyte with two CV scans between 1.15 V and 0.0 V (RHE) with 10 mV s<sup>-1</sup> and 1500 rpm. Subsequently, two scans with 900 rpm followed. Then the electrolyte was saturated with nitrogen and the catalyst was cycled 20 times with a sweep rate of 300 mV s<sup>-1</sup> followed by a scan with 100 mV s<sup>-1</sup> and a scan with 10 mV s<sup>-1</sup>. The last named scan is required for the correction of the capacity contribution from the scans in oxygen-saturated electrolyte.

The kinetic current density  $j_{kin}$  was determined from the capacity-corrected CV in O<sub>2</sub>-saturated electrolyte at 1500 rpm according to the following equation:

$$j^{-1} = j_{kin}^{-1} + j_{diff}^{-1} \tag{1}$$



**Fig. 1** RDE curves of the pure and poisoned catalysts (**a**-**c**) for 1500 rpm, 10 mV s<sup>-1</sup>, in 0.1 M H<sub>2</sub>SO<sub>4</sub> Category plots of kinetic current densities at 0.75 V for the original (filled) and poisoned catalysts (hatched). Bars indicate the error of the electrochemical experiments (**d**)

Averages and errors were determined from the two scans of each measurement and two measurements per sample. The effect of poison was evaluated by comparing the kinetic current densities  $j_{kin}$  at 0.75 V (RHE). The diffusion limited current density  $j_{diff}$  was read from the diffusion plateau of the capacity-corrected RDE curve (see Fig. 1).

# 2.4 57 Fe-Mößbauer spectroscopy

The Mößbauer measurements were performed in transmission mode with a 100 mCi  $^{57}$ Co/Rh source and a scintillation detector. Samples were prepared and measured under standard conditions in a velocity range of  $\pm$  6 mm s<sup>-1</sup> and the isomer shifts were determined relative to  $\alpha$ Fe foil at 298 K. The collimators before and after the sample holder were adjust to 3 and 5, respectively. All Mößbauer spectra were fitted using the program Recoil.

## 3 Results and discussion

In order to identify the activity changes induced by sulfite-treatment the ORR activity of the original and poisoned catalysts were measured.

In Fig. 1 the RDE curves of the original and poisoned catalysts are shown for HT600HCl (a), HT800HCl (b) and HT800HCl+S (c). The treatment with sodium sulfite has two effects: The diffusion limiting plateau is lowered and the onset potential for ORR is shifted to smaller potentials. The diffusion limiting current density depends on different parameters (that remain constant for all our experiments) and the number of transferred electrons



Fig. 2 Models for the deactivation of FeN<sub>4</sub> sites by anion binding: **a** the anion binds to protonated sites in the vicinity, **b** and **c** the anion interacts with the active site, while in **b**) the ORR is still possible, the active site is completely deactivated in **c**)

 $n_e$ . For the oxygen reduction reaction a direct reduction to water with  $n_e = 4$  and an indirect reduction to hydrogen peroxide with  $n_e = 2$  are possible. The lowering of the diffusion limiting current density could therefore indicate that the selectivity is shifted toward the formation of the undesired product of hydrogen peroxide.

The shift in onset potential causes a lowering of the ORR activity as it becomes apparent when the category plot of the kinetic current densities for the three catalysts are compared in Fig. 1d. The loss of activity is most pronounced for HT600HCl followed by HT800HCl and lowest for HT800HCl+S.

As described in the introduction, Herranz et al. [22] showed that 80 % of the activity attributed to the recovered state were lost by anion binding. Further it was discussed that the anion binding took place on protonated nitrogen species in the vicinity of active sites. This interpretation was based on the comparison of Mößbauer spectra of the catalyst in the deactivated state (0.1 mA cm<sup>-2</sup>) and reactivated state (0.5 mA cm<sup>-2</sup>), the spectra were almost similar.

Please note, for HT600HCl and HT800HCl, the final step of preparation was an acidleaching. Therefore, these two catalysts can only be prone to an additional loss of activity induced by sulfite ions as all protonated sites should be already blocked by anions. The extend of it is similar to Herranz et al. for HT600HCl and less for the two samples prepared at 800 °C.

In Fig. 2a a model is shown how the deactivation according to Herranz et al. take place: the turn-over frequency is lowered as protonated groups in the vicinity cannot accelerate the reaction anymore. Beside this two further possibilities might appear. In Fig. 2b the anion binds as axial ligand to the active site, but still the interaction with oxygen is possible. Due to electronic changes the turn-over frequency will change. In contrast to this, Fig. 2c should indicate that the interaction with the anion is as strong that the active site cannot interact with oxygen anymore. Therefore, this site would be completely deactivated, whereas in a) and b) only the turn-over frequency will change.

It becomes clear from Fig. 2 that the deactivation mechanism via the anion adsorption on protonated sites in the vicinity should give no changes in Mößbauer spectroscopy while changes of the Mößbauer parameters are expected in case of b) and c). In order to investigate the impact of sulfite anions on the iron signature of our catalysts Mößbauer spectroscopy was performed.

The sulfur free original catalysts were fitted assuming the presence of three different FeN<sub>x</sub> sites as previously identified for Fe-N-C catalysts [6, 7, 12], whereas for the

					HT600HC1	Area / %	HT800HCI	Area / %	HT800HCl+	-S Area / %
	$\delta_{\rm iso}$ / mm s <sup>-1</sup>	$\Delta E_Q$ / mm s <sup>-1</sup>	fwhm / mm $s^{-1}$	$H_0 / T$	oc	Ч	OC	Ь	oc	Ь
S1	-0.11 (0.01)	I	0.38 (0.02)	I	I	I	19.2 (0.8)	15.0 (0.2)	I	I
D1	0.36 (0.02)	0.89 (0.07)	$0.6^{*1}$	Ι	66.6 (0.7)	51.6 (0.7)	42.2 (3.0)	30.5 (0.6)	35.4(1.1)	42.5 (0.4)
D2	0.31 (0.07)	2.69 (0.34)	$1.0^{*}$	I	17.6 (0.6)	29.2 (1.0)	16.7 (1.5)	25.1 (1.2)	35.4 (1.3)	31.8 (0.7)
D3	0.38 (0.03)	1.66 (0.23)	0.8*	Ι	15.9(0.6)	3.2 (1.1)	15.6 (2.9)	19.0 (0.8)	Ι	Ι
D4	0.98 (0.02)	2.58 (0.04)	0.7*		Ι	Ι	I	I	16.9(1.0)	12.2 (0.8)
DP	As reported in <b>7</b>	Table 2								
Sext1	0.40 (0.37)	I	0.38 (0.04)	31.9 (1.1)	Ι	Ι	6.4 (1.7)	4.5 (0.5)	6.0(1.2)	3.2 (0.6)
Sext2	1.06 (0.01)	I	0.28 (0.04)	9.8 (0.09)	I	I	I	Ι	6.4(1.3)	7.5 (0.8)
<sup>1</sup> Parame	eters with * were so	et constant								

 Table 1
 Mößbauer parameters of the different iron sites

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Fig. 3 Mößbauer spectra of the Fe-N-C-HT800HCl in its original form (a) and after poisoning (b)

DP	$\delta_{\rm iso}$ / mm s <sup>-1</sup>	$\Delta E_Q$ / mm s <sup>-1</sup>	fwhm / mm s $^{-1}$	area / %
HT600HC1	0.68	2.40	0.38	3.2
	(0.03)	(0.05)	(0.1)	(1.1)
HT800HCl	0.79	2.48	110	5.9
	(0.01)	(0.12)	(0.26)	(2.2)
HT800HCl+S	1.2	1.94	0.34	2.2
	(0.03)	(0.06)	(0.14)	(0.8)

Table 2 Mößbauer parameters of the poisoned species

HT800HCl+S catalyst also ferrous iron sulfide sites were found. In addition, to some extend inorganic iron species were present in some of the catalysts. The Mößbauer parameters are summarized in Table 1.

For all poisoned catalysts the same iron species as in the original catalyst were assumed to be present, and only absorption areas allowed to change (compare Table 1). In addition, to address the formation of a possible Fe-site attributed to poisoning a fourth symmetric doublet (DP) was added that was allowed for all parameters to change.

Exemplary, Fig. 3 shows the fitted Mößbauer spectra of the original and poisoned HT800HCl catalysts. In the following, we first like to focus on the Mößbauer spectrum of the original catalysts. Up to five different species were identified in the different catalysts.

S1 and Sext1 are related to superparamagnetic iron and alpha-iron, respectively [12, 29, 30]. D1 is related to ferrous FeN<sub>4</sub> moieties in the low-spin state, these were previously identified as ORR active sites [6, 7]. A second doublet (D2) is related to FeN<sub>4</sub> with a structure similar to FePc with ferrous iron in the mid-spin state [8]. The third doublet D3 might be identified as CFeN<sub>2</sub> or a charged FeN<sub>4</sub>-like site [23, 31]. For the sample which already contains sulfur (HT800HCl+S) two additional iron sites (D4 and Sext2) were found. As discussed in Janßen et al. [28] these sites are both assigned to iron sulfide (Fe<sub>3</sub>S<sub>4</sub>) nanoparticles.



Fig. 4 a Comparison of the original and poisoned catalyst Fe-N-C-HT800HCl after normalization for the Sext1 intensity and b difference spectra for all three catalysts as indicated

Induced by the poisoning treatment a fourth doublet appears in the spectra denoted as DP. The Mößbauer parameters assigned to this doublet are compared for the three catalysts in Table 2. Comparing the absorption areas of the D1 site in the original and poisoned catalysts it can be concluded that the relative loss of the absorption area accounts for 30 % and 27 % for HT600HCl and HT800HCl, respectively. Hence, not all ORR active sites are blocked. This is in agreement with only a partial loss of ORR activity and the fact that the utilization factor of ORR active sites is often  $\ll 100 \%$  [20]. However, in case of HT800HCl+S an increase by 20 % can be recognized. This will be discussed later.

The spectra of the original and poisoned catalyst are overlaid in Fig. 4a after normalization to the sextet intensity. As this species remained in the catalyst even during the acid-leaching (as part of the preparation), it is assumed that also the poisoning treatment will not change the concentration of this species. Clear difference between the pure and the poisoned catalyst can be seen.

In Fig. 4b the difference spectra of the original catalyst minus the poisoned catalyst are shown for all three investigated catalysts. For both carbon-supported samples the formation of the new doublet DP is visible in terms of a negative contribution in the difference spectra. In addition, the lowering of the D1 species is indicated by the positive contribution.

As mentioned above, the S-added catalyst behaves nearly opposite to the other two catalysts. Eventually, this might be caused by the different preparation. Three main differences are identified: i) the alternative Fe-N-precursor in comparison to the porphyrin, ii) a heat-treatment as final preparation step of this catalyst and iii) the presence of sulfur in the precursor mixture.

As the active site seems to be similar for alternatively prepared catalysts [9, 13, 20] compared to porphyrin-based ones, an effect of the Fe-N-precursor is excluded. For catalysts where the preparation ends with a heat-treatment step in general a recoverable activity decay can take place and a deactivation by sulfite ions. Hence, any impact of the heat-treatment as final preparation step on the different behavior cannot be excluded. Furthermore, as

	$I_2^*$	HSO <sub>4</sub> *	Br*	Cl*	HT600HCl	HT800HCl	HT800HCl+S
$\delta_{\rm iso}$ / mm s <sup>-1</sup>	0.18	0.08	0.11	0.20	0.68	0.79	1.18
$\Delta E_Q$ / mm s <sup>-1</sup>	3.3	3.28	3.16	2.75	2.40	2.48	1.94

**Table 3** Comparison of Mößbauer parameters observed for different axial ligands to ferrous  $FeN_4$  sites.Data indicated with \* were taken from Taube [23] and Kramm [24]

HT800HCl+S already contain S-species it could be that it is not as sensitive to a poisoning treatment with sulfite ions as the other two S-free catalysts. One possible interpretation would mean that HT800HCl+S is already in a "deactivated" state due to the presence of S-species. A more detailed study will be required to elucidate the overall effect of sulfide and sulfite species during catalyst preparation and/or electrochemistry on the performance of the catalyst.

How to assign the newly formed DP doublet?

As explained in the introduction Taube [23] investigated the effect of anion binding to molecular FeN<sub>4</sub> moieties. It was found that new doublets compared to the fourfold coordinated FePc were formed induced by anion binding in axial direction. The quadrupole splitting was increasing with decreasing ligand field strength of the anion.

In Table 3 the anions investigated in Taube's work and the corresponding Mößbauer parameters are listed and compared to the values obtained for the sulfite species in our work (Note: isomer shift in Taube was reported vs.  $Na_2[Fe(CN)_5NO]\cdot 2H_2O$  and is transferred to alpha iron reference in this work) [23]. Further the parameters found in Kramm for the interaction of FeN<sub>4</sub> sites with HSO<sub>4</sub> in porphyrin-based Fe-N-C catalysts are added [24].

According to the spectrochemical series the ligand field strength for the anions of relevance to Table 3 increases in the order I <  $HSO_4$  < Br <  $S^{2-}$  <  $Cl \ll SO_3^{2-}$ . Comparing the different anions it becomes clear, that all anions investigated by Taube and Kramm are weak ligands.

Therefore, ferric high-spin complexes are formed by their interaction with the  $FeN_4$  sites. In contrast, the ligand field strength of sulfite is significantly more pronounced so that a low-spin state is expected. In this work, the poisoned iron species (DP) remains in the ferrous state as the original ORR active iron sites. Induced by sulfite treatment; however, the spin state is changed from low- to high-spin state. This indicates that most probably the parameters of the doublet assigned to the poison treatment are similar for HT600HCl and HT800HCl, significant different values are found for HT800HCl+S.

Why do the Mößbauer parameters of the doublet DP assigned to the interaction of sulfite anion differ for the porphyrin-based catalysts compared to the S-added alternatively prepared catalyst?

A possible explanation to this might be found in the ambident character of the anion. In Fig. 5 possible coordination of the sulfite anion to the  $FeN_4$  center are shown. Based on the characteristics for oxygen and sulfur ligands it is assumed that the ligand field strength increases from left to right. In addition, the electric quadrupole interaction is assumed to be smaller for the symmetrically attached options (Fig. 5b, d) in comparison to options in Fig. 5a and c.

Based on these considerations, we assume a coordination similar to Fig. 5c for the two porphyrin based catalysts while for HT800HCl+S the fourth option (Fig. 5d) seems most likely.

Consequently, the electron density and the anisotropy at the metal center would change causing variations of the Mößbauer parameters as observed in this work.



Fig. 5 Possible axial binding of sulfite species to  $FeN_4$  sites. The square-planar coordination of iron by nitrogen atoms is indicated in the schemes by ellipses

According to the possibilities of active site poisoning by anion binding, it is most likely that the anion binds directly to the active sites. However, based on our results it is not possible to distinguish between the two options of a lowered turn-over frequency (indicated in Fig. 2b) or a complete deactivation of FeN<sub>4</sub> sites that adsorb sulfite (Fig. 2c).

In addition, the integration of sulfite groups in the carbon matrix could cause additional electronic changes that might affect the ORR activity of these catalysts.

#### 4 Conclusion

In this work the effect of sulfite ions on the ORR activity and structural constitution of Fe-N-C catalysts was investigated for three differently prepared Fe-N-C catalysts.

The porphyrin-based catalysts reveal a relatively homogeneous composition with only  $FeN_x$  sites (for HT600HCl) or low quantity of inorganic iron species (HT800HCl). In contrast HT800HCl+S that was prepared from different precursors and by S addition shows  $FeN_4$  species and iron sulfide. Eventually the presence of iron sulfide affects the interaction of this catalyst with sulfite.

It is found that the degree of deactivation induced by anion binding is different for porphyrin-based catalysts compared to the alternatively prepared, S-added catalyst. Similarly, also the observed changes in the Mößbauer spectra differ. The catalysts reveal the presence of a new doublet that seems to be assigned to an axial ligation of sulfite to FeN<sub>4</sub> sites. Two different options for the ligation of sulfite are proposed and assigned to the ambident character of the ion.

As all catalysts still contain the ORR active  $FeN_4$  sites assigned to D1 and display some catalytic activity, it is difficult to say whether those anion-blocked sites are deactivated or significantly lowered in their turn-over frequency.

**Acknowledgments** Financial Support by the German Federal Ministry of Education and Research (BMBF) via the contract 05K16RD1 is gratefully acknowledged. In addition to this, IM, AS and UIK like to acknowledge financial support by the German Research Foundation (GSC1070).

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