

On Active-Site Heterogeneity in Pyrolyzed Carbon-Supported Iron Porphyrin Catalysts for the Electrochemical Reduction of Oxygen: An In Situ Mössbauer Study

A. L. Bouwkamp-Wijnoltz, W. Visscher, and J. A. R. van Veen

Schuit Catalysis Institute, Eindhoven University of Technology, P. O. Box 513, Eindhoven, The Netherlands

E. Boellaard and A. M. van der Kraan*

Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, Delft, The Netherlands

S. C. Tang

Shell DevCo, Westhollow Technology Centre, Houston, Texas

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Some FeTPP–Cl/carbon electrocatalysts, heat-treated at temperatures up to 800 °C, have been studied with cyclic voltammetry, x-ray photoelectron spectroscopy, extended X-ray absorption fine structure, and in situ Mössbauer spectroscopy. It appears that the heat treatment induces considerable site heterogeneity in electronic terms, although structurally the Fe–N₄ moiety seems persistent. The data indicate that only part of these Fe–N₄ sites contributes to the activity for the electrochemical reduction of O₂ but that they operate according to the well-known redox mechanism.

Introduction

Carbon-supported transition metal (TM) N₄ macrocyclics are well-known catalysts for the electrochemical reduction of oxygen, with possible application in a direct methanol fuel cell with an acidic electrolyte since they are not poisoned by methanol. For this purpose, the TM complexes are adsorbed onto a support like carbon black or activated carbon and heat-treated (at rather elevated temperatures, 500–800 °C) in an inert atmosphere to increase the activity, selectivity, and stability of the catalysts. The structure of the active site generated by such a heat treatment has been the subject of some debate, and there appears to be a growing consensus that at the optimum pyrolysis temperatures the metal chelate has lost its aromatic ring structure but has retained its Me–N₄ core, which constitutes the active site.^{1–7} However, other ideas continue to be canvassed; indeed, recently, Bae et al.,⁸ in a fine in situ Fe–K edge X-ray absorption near-edge (XANES) study, adduced further evidence for their view that it is a TM in a non-N₄ environment that is the active site for oxygen reduction. We think that this view is mistaken⁹ and would like to present some further evidence here, arguing in particular that all non-Fe–N₄ species that may be generated in the pyrolysis step can be removed from the catalyst without impairing its electrocatalytic activity. The nature of the active sites generated at still higher temperatures and/or in the presence of NH₃ is not addressed here.^{10,11}

Another point that Bae et al.⁸ bring up is the site heterogeneity in heat-treated carbon-supported iron porphyrins. It is indeed the case that usually the active site population is seen as pretty homogeneous, even in heat-treated catalysts, but this turns out to be completely unwarranted. This point was also addressed in A.L.B.-W.'s Ph. D. project by means of Mössbauer spectroscopy,¹² and we would like to present the pertinent data in this paper.

It seems natural to conceive of the reduction of oxygen on these carbon-supported TM chelates in terms of a redox

mechanism,^{13–15} in that a TM needs to be in its two valent state to be able to accept an oxygen molecule. This mechanism is not universally admitted, though,¹⁶ and indeed, it is worrisome that in cyclic voltammetry (CV) only a fraction of the macrocyclics present seem to be electroactive and that, especially in nonpyrolyzed catalysts, the apparent Fe(2⁺)/Fe(3⁺) redox potential is so low that it is difficult to see how it can be active at the much higher O₂ reduction potentials. We have tried to shed some light on this problem through in situ Mössbauer spectroscopy, and the results obtained will be discussed herein.

This paper, then, presents ex situ and in situ ⁵⁷Fe Mössbauer absorption spectroscopy data, supported by some X-ray absorption spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements, on FeTPP–Cl adsorbed on high surface area carbon black and heat-treated at various temperatures—these data indicate (i) that the majority of Fe present is electroactive, although for a large part the electron transfer kinetics may be very slow, (ii) that something similar to the original Fe–N₄ moiety continues to be the site of the O₂ reduction activity, even after a heat treatment at temperatures as high as 800 °C, but (iii) that the central Fe ion exists in a variety of electronic states, and (iv) that the Fe(2⁺) state is in fact accessible at O₂ reduction potentials.

Experimental Section

Undoped FeTPP–Cl was obtained from Aldrich. ⁵⁷Fe-enriched FeTPP–Cl was prepared using a method adapted from refs 17–19 as follows:

First, tetraphenylporphyrin, H₂TPP, was prepared applying the Adler method using refluxing propionic acid.²⁰ The chlorin impurity was removed using 2,3-dichloro-5,6-dicyano-benzoquinone,²¹ and the H₂TPP was purified by dry column chromatography, using alumina and CH₂Cl₂ as eluent, followed by precipitation from the concentrated eluted solution through the addition of methanol. Then, 33.5 mg of ⁵⁷Fe was dissolved in

12 mL of refluxing acetic acid and 1 mL of acetic acid anhydride, under argon. Still under argon, the freshly made Fe(2⁺)-acetate solution was added to a solution of 372 mg of H₂TPP and 140 mg of NaCl in 30 mL of CH₂Cl₂. The reaction mixture was brought to reflux, and argon was replaced with oxygen. After 1 h, the solvent was removed, and the resulting solid was dissolved in 250 mL of CH₂Cl₂; 200 mL of concentrated HCl was added, and the mixture was stirred magnetically for 1 h. The solvent was again removed, and the product was dissolved in CHCl₃, to which hot methanol was added. After the product was cooled, dark crystals of ⁵⁷FeTPP-Cl formed. These were filtered off and dried at 125 °C/2 Torr; yield, 410 mg (93%).

Vulcan XC-72R was chosen as carbon support. Catalysts were prepared by loading 7 wt % FeTPP-Cl, corresponding to about 80–90% of a monolayer (assuming a flat adsorption geometry), on the Vulcan support. This was achieved by dissolving the appropriate amount of chelate in CHCl₃, suspending the carbon in this solution, and adding hexane slowly, under magnetic stirring, until adsorption was completed (as judged from the total disappearance of color from the solution).

Heat treatment was carried out in a down-flow reactor in an argon atmosphere, deoxygenated using a Cu tower at 125 °C. The argon flow rate was 25 mL/min. A heating rate of 10 °C/min was applied and a dwell time at the final temperature of 2 h. The sample was cooled to room temperature in argon as well.

In some cases, a heat-treated catalyst was “acid-washed”, i.e., treated with 0.5 M H₂SO₄ at 80 °C for 10–15 min, followed by extensive rinsing with water. The Fe content before and after this acid wash was determined by atomic absorption spectroscopy (AAS) after total destruction of the sample (by heating 50 mg of catalyst, 2.5 mL of concentrated nitric acid, and 7.5 mL of concentrated sulfuric acid for 2 h at 150 °C in a Teflon cup in a metal holder). Nitrogen elemental analysis was performed at TNO Zeist and Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany).

All electrochemical measurements were performed in conventional three electrode setups, as described previously.^{15,22} Activity measurements employed the floating electrode technique²³ in which Teflon-bonded catalysts (20 wt % Teflon, ex Fluon GP-1 from Du Pont, in the final dry electrode) applied on an 80 mesh gold screen were positioned horizontally such that it just contacted the (oxygen-saturated) electrolyte (details in ref 22). CV was mainly performed on Leit C electrodes, employing a gold rotating disk electrode with a hollow cavity, about 2 mm in depth. This cavity was filled with “Leit C”, a conducting carbon cement obtained from Neubauer Chemicals, to which the catalyst was applied by dipping the electrode with fresh paste in a small amount of catalyst, followed by drying, wetting with ethanol, and thorough rinsing with water (details in ref 15). The AC voltammetry with such electrodes was carried out at the University of Twente, employing the equipment described in ref 24.

Both ex situ and in situ Mössbauer experiments were performed using the ⁵⁷Fe-enriched FeTPP-Cl material. For the in situ experiments, an electrochemical cell as shown in Figure 1 was used. It allowed experiments in oxygen- and argon-saturated solutions. A mercury-sulfate electrode (MSE) was used as a reference electrode. Its compartment was connected to the cell via an agar-agar salt bridge. The electrolyte was 0.5 M H₂SO₄. The electrolyte layer was minimized by two thin silicon spacers. The working electrode was made of Teflon-sintered catalyst (100 mg of catalyst, 16 wt % Teflon, cured at the standard temperature of 325 °C). The current collector was

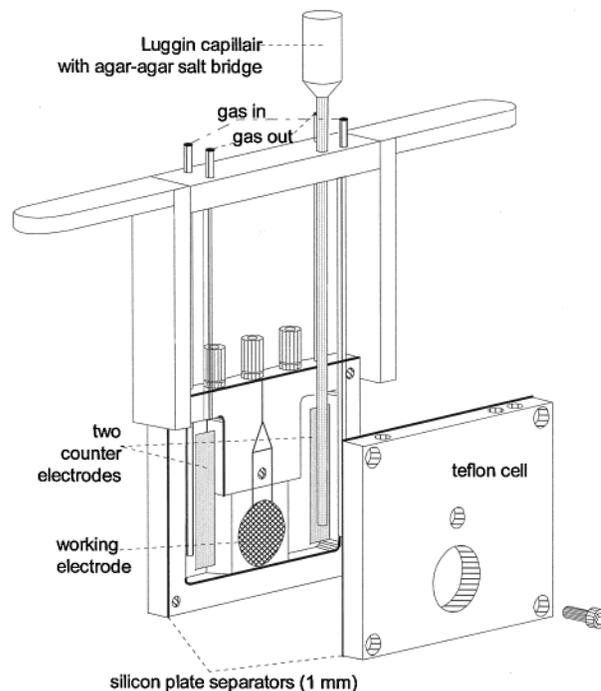


Figure 1. In situ Mössbauer cell.

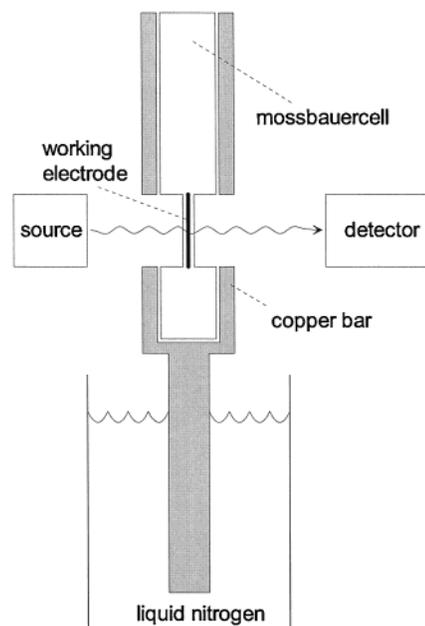


Figure 2. Experimental setup during Mössbauer experiments.

platinum in the form of a coarse mesh screen. The cell contained two electrolyte compartments. Laminar flow of the electrolyte was achieved by blocking one of the gas out flows, and in this way, complete penetration of the electrode with electrolyte was accomplished. If the electrolyte was not flowed through every now and then during argon saturation, traces of oxygen remained inside the working electrode. Two platinum counter electrodes were used to ensure a reasonable current distribution. The counter electrodes were interconnected. For the potential-dependent measurements, the potential was scanned with 1 mV/s from the open-circuit potential (OCP) to the desired potential. The Mössbauer experimental setup is given in Figure 2. For the potential-dependent measurements, the cell was quickly cooled to liquid nitrogen temperature (77 K). As soon as the electrolyte resistance reached a high value, indicated by the

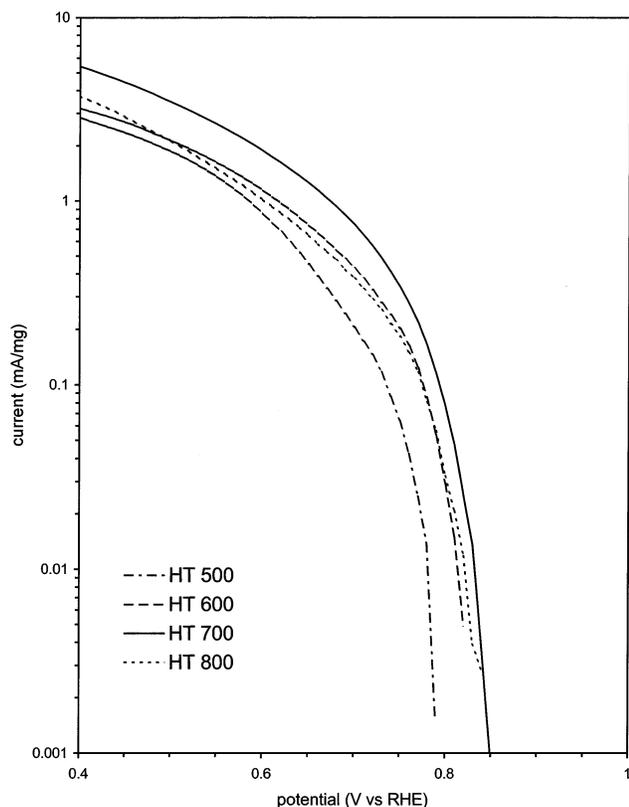


Figure 3. Oxygen reduction at 7 wt % FeTPP-Cl/Vulcan heat-treated at different temperatures. Floating electrodes, 0.5 M H₂SO₄, 1 mV/sec.

overload signal of the potentiostat, the latter was turned off and the leads were disconnected from the cell. This procedure was taken from Fierro et al.²⁵ who opined that the situation at the electrode remained intact this way. Because of the position of the cell, outside the cryostat, the temperature could not be maintained at 77 K, but it slowly rose to about 130 K, which then, however, remained rather constant during the experiment.

Room temperature EXAFS (extended X-ray absorption fine structure) measurements were performed at Station 9.3 of the Daresbury Synchrotron Radiation Source operating at an energy of 2.0 GeV and an average current of 250 mA. The data were taken in the fluorescent mode using a Si(220) double crystal monochromator, and for iron, the K edge at 7.11 keV was used. The data were analyzed with the XDAP package, version 2.2.2.²⁶ Some XPS measurements were carried out at Shell Research and Technology Centre, Amsterdam, making use of a Kratos XSAM 800 instrument.

Results and Discussion

Overall Structure of the Active Site. The oxygen reduction activity of FeTPP-Cl/Vulcan, heat-treated at various temperatures, is shown in Figure 3. As expected, the activity increases with heat treatment temperature up to 700 °C, but heating at 800 °C does not lead to a further increase in activity—rather, a decrease is observed. When these catalysts are measured with a rotating ring-disk electrode (RRDE) setup, it is observed¹² that the selectivity to H₂O₂ remains approximately constant, in agreement with ref 6, suggesting that no major changes in active site configuration occur.

In the case of CoTPP/carbon electrocatalysts, previous EXAFS data concerning the effect of the pyrolysis on the local Co structure show that up to and including the optimum (optimum in terms of observed catalytic activity) pyrolysis

TABLE 1: Fe-K Edge EXAFS Data for FeTPP-Cl/Vulcan by Fitting in the R-Space until a Satisfactory Fit Is Obtained for the *k*¹-Weighted Fourier Transform Functions^a

catalyst	first shell Fe-N				second shell Fe-C			
	<i>N</i>	<i>R</i>	$\Delta\sigma^2$	ΔE	<i>N</i>	<i>R</i>	$\Delta\sigma^2$	ΔE
fresh	4.2	2.047	0.00214	0.07	8.2	2.971	0.00007	15.1
HT 325	3.3	2.056	0.00359	-0.07	8	3.044	0.00046	7.6
	(4.0 ^b)	(2.044)	(0.00712)	(1.31)	(3.025)	(0.000)	(9.8)	
HT 700	4.1	1.925	0.0100	11.6				

^a *N* = coordination number ($\pm 20\%$), *R* = interatomic distance (± 0.02 Å), $\Delta\sigma^2$ = Debye-Waller factor (in Å² $\pm 20\%$), and ΔE (in eV $\pm 20\%$). ^b As the value for *N* of the first coordination shell is fixed to 4.0 in the case of sample HT 325, the deduced values are presented between brackets.

temperature, the Co-N₄ moiety remains substantially intact;³ indeed, it appears that when Co ions and a suitable N donor (e.g., 2,5-dimethylpyrrole) are added to the carbon support and it is heated at the optimum temperature of 700 °C, the Co-N₄ configuration forms spontaneously.²² At still higher temperatures, decomposition of also this central part of the macrocyclic is observed, with a concomitant loss in activity.³ To verify if this picture also pertains in the case of FeTPP-Cl/carbon, three samples (fresh, HT 325, and HT 700) were examined with XAS.

The analysis results of the iron K edge EXAFS data for these three FeTPP-Cl/Vulcan samples are summarized in Table 1. The Fe-N and Fe-C coordinations analyzed for the fresh sample are consistent with the FeTPP-Cl crystal data,²⁷ strongly suggesting that the porphyrin adsorbs intact. On the other hand, it is curious that there is no sign of the Cl ligand, the more so as Cl is clearly present according to XPS, and the ⁵⁷Fe Mössbauer spectrum of the fresh catalyst is identical to that of crystalline FeTPP-Cl (vide infra). Perhaps some variation in the Fe-Cl interatomic distance is induced upon adsorption, sufficient to make it disappear from the EXAFS spectrum.

After a heat treatment at 325 °C—the curing temperature of Teflon-bonded electrodes—the structure around the Fe has changed only slightly, indicating that although largely intact the porphyrin is starting to interact with the subjacent carbon more strongly than before. This phenomenon is probably due to redispersion of initially formed porphyrin crystallites, leading to a more monolayer-like active phase (see below). The first shell coordination number does appear to be a bit low at 3.3, but constraining it to 4.0 does not visibly impair the fit (Table 1). The optimum heat treatment temperature of 700 °C obviously has a much stronger impact. The EXAFS results indicate by the large values of $\Delta\sigma^2 = 0.01$ and $\Delta E = 11.6$ an increase in static and/or dynamic disorder of the local structure of the iron site. This increase in disorder of the local structure is most probably due to the removal of the periphery of the macrocyclic ligand (structure beyond the first shell could not be determined). Nevertheless, the first shell still appears to be Fe-N₄, but the interatomic distance has contracted to 1.93 Å, becoming similar to that observed for Co-N₄, 1.90 Å, indicating that where Fe sits above the porphyrin plane in intact FeTPP-Cl, it has moved in-plane upon the destruction of the periphery of the macrocyclic ligand. However, given the large disorder, it cannot be absolutely excluded that other Fe sites than Fe-N₄ exist in the HT 700 catalyst. Whether some Fe support bond has been formed, as hypothesized earlier,²⁸ must also remain moot.

If, then, the Fe-N₄ moiety remains largely intact upon a heat treatment at 700 °C, we should expect that hardly any Fe would be lost upon acid washing, and in fact, only ~15% of the Fe is lost after the H₂SO₄ treatment at 80 °C. When, however, we do the heat treatment at 800 °C, the picture changes dramatically.

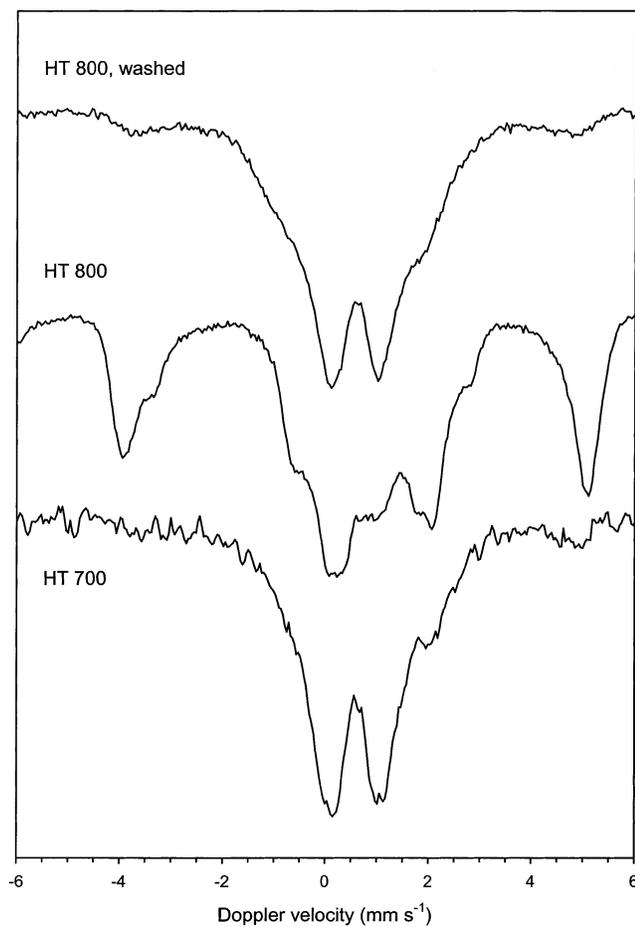


Figure 4. Result of the acid treatment, ex situ Mössbauer spectra, 300 K.

Now, 40% of the Fe can be dissolved from the surface, and the question is whether this Fe is involved in some way in active site formation as Bae et al.⁸ claim or whether it represents an inactive fraction. From the ex situ Mössbauer spectra in Figures 4 and 5, we deduce that (i) after a heat treatment at 800 °C the spectrum is dominated by a species, a magnetic iron oxide phase (presumably formed from metallic Fe, which should be the primary pyrolysis product upon chelate destruction, through air exposure), that is completely absent after the 700 °C treatment and (ii) an acid wash removes this oxidic species nearly completely, to leave a Mössbauer spectrum that closely resembles the one obtained after 700 °C heating, which on the basis of the EXAFS results, corresponds to some Fe–N4 species.

As the oxygen reduction activities of FeTPP–Cl/Vulcan HT 800 and its acid-washed counterpart turn out to be virtually identical,¹² one cannot but conclude that the Fe species that form upon destruction of the porphyrin ligand are lost to catalysis, which is dependent on the intact cores of the original chelate.

An overview of the ex situ Mössbauer spectra is given in Figure 5. As mentioned above, the spectrum of the fresh catalyst is identical to that of the FeTPP–Cl powder itself, which in turn is in accordance with published data.^{18,19,21} A (apparent) singlet is observed, due to spin–spin relaxation phenomena that result in magnetic broadening.²⁹ Treating FeTPP–Cl/Vulcan at low temperatures (225, 325 °C) already changes its spectrum, which indicates that even in this temperature range the environment of the iron center is already affected. The change is probably connected with the redispersion of the porphyrin (see discussion in the next section). After the 325 °C treatment, the

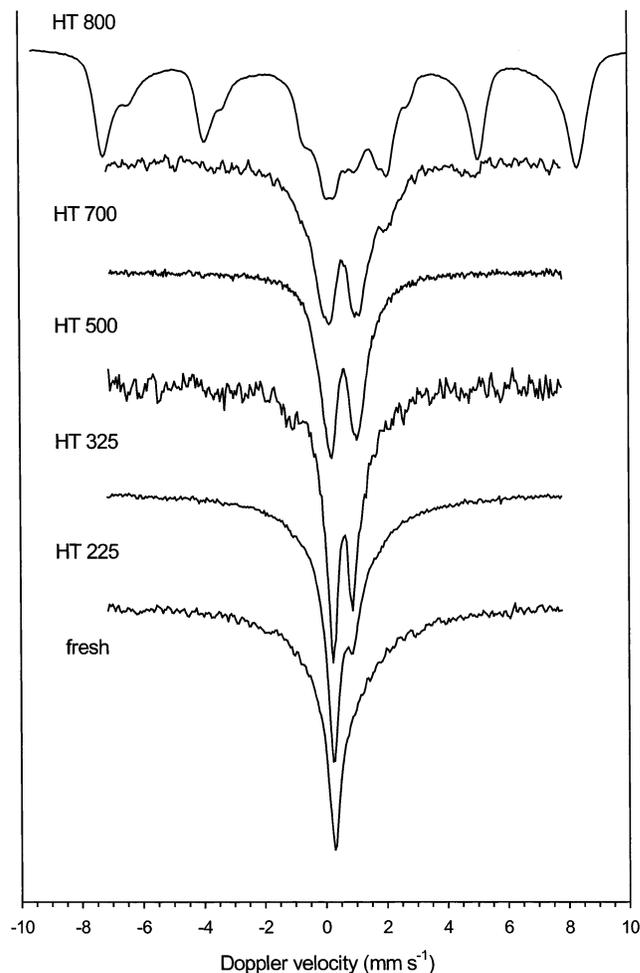


Figure 5. Ex situ Mössbauer spectra of 7 wt % ⁵⁷FeTPP–Cl/Vulcan heat-treated at different temperatures, 300 K.

original FeTPP–Cl spectrum still accounts for ~25% of the observed spectrum. Increasing the pyrolysis temperature results in spectra with broad lines due to a variety of doublets. The HT 500 and HT 700 spectra, which are somewhat different from those obtained previously for on the face of it comparable samples^{28,30} for unknown reasons, will be further discussed below. On the basis of the broad lines, it is already clear, however, that a lot of heterogeneity has been induced at the iron sites. This means that while the overall structure of the iron site remains close to the original Fe–N4 moiety (on the basis of the EXAFS results), there must be substantial local variation in how this unit is attached to the subjacent carbon carrier.

Cyclic Voltammetry (CV). The evolution of the redox properties of FeTPP–Cl/Vulcan as the heat treatment temperature increases was at first studied with CV. The CVs of the fresh and HT 325 catalysts are compared in Figure 6. Both show the same redox transition at 0.2 V vs RHE, which has been assigned to the Fe(2⁺)/Fe(3⁺) transition of adsorbed FeTPP–Cl.²⁴ Although the peak position does not change, the signal is much stronger for the HT 325 sample. This is due, we believe, to redispersion of the chelate, implying that our preparation method of forced adsorption in this case has led to small crystallites: on one hand, it is observed in XPS that the N signal for the HT 325 sample is stronger than for the fresh one (0.76 vs 0.30 at %), which can only be rationalized by assuming that redispersion of initially formed crystallites has occurred; on the other hand, while a physical mixture of FeTPP–Cl and Vulcan

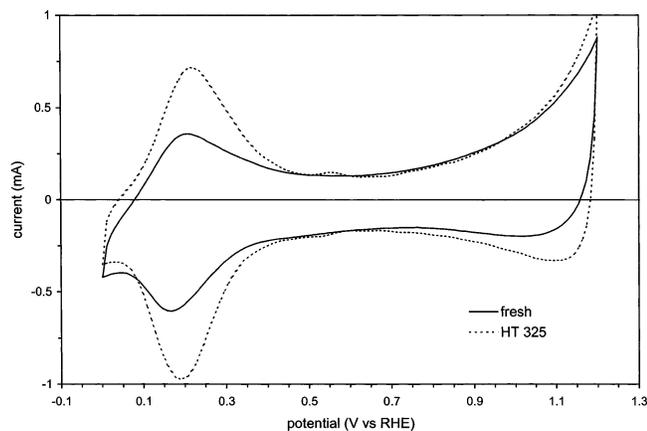


Figure 6. Cyclic voltammograms of fresh and HT 325 7 wt % FeTPP-Cl/Vulcan. Leit C electrodes, argon-saturated 0.5 M H₂SO₄, 100 mV/sec.

as such does not show a redox transition, after a heat treatment at 325 °C a (small) redox peak becomes visible. In terms of the effectiveness of the pyrolysis process, this redispersion is a good thing, as superactive site formation starts from the chelate in monolayer form.^{9,17,29}

It has been observed before that only a fraction of the chelate adsorbed on a carbon carrier turns out to show up in CV.^{8,25,32} (That is, the charge corresponding to the redox transition seen in CV is much less than the charge expected if all chelate molecules present in the electrode would contribute to the signal.) In the present case, it is only of the order of 10%. The reason behind this relative invisibility is unknown—perhaps it is related to inhomogeneity in the carbon support, inasmuch as it has been shown that electron transfer rates are very slow for the basal planes of graphite (HOPG) and can be greatly improved by the introduction of surface defects.³² As will be shown below in the paragraph of in situ Mössbauer experiments, a much larger fraction is electroactive than appears from the CV. For the moment, however, we will take the visible fraction as representative.

The cyclic voltammograms obtained for FeTPP-Cl/Vulcan after various heat treatment temperatures, from 325 to 700 °C, are shown in Figure 7. It appears that the position of the redox transition slowly moves to higher potentials with increasing HT temperature and that its intensity continuously decreases, to disappear in the HT 700 sample. The latter could simply be due to peak broadening, preventing the redox current from rising above the background charging current, and so, we turned to AC voltammetry. As Figure 8 shows, the evolution of the redox transition(s) can now be followed till the highest HT temperatures. The original Fe(2⁺)/Fe(3⁺) transition slowly moves from about 0.2 V vs RHE in the fresh catalyst to about 0.4 V vs RHE in the HT 700 one; after an 800 °C treatment, however, it can no longer be clearly distinguished. Beginning with the HT 500 sample, a second redox transition is in evidence, at about 0.9 V vs RHE, which appears to broaden quite substantially and to shift to lower potentials in the HT 700 and 800 samples. At present, we cannot definitely assign this transition, but we tend to think that it may be due to a ligand transition; in the intact porphyrin, the TPP/TPP⁺ transition occurs at about 1.2 V vs RHE, and the partial destruction of the porphyrin ligand, with concomitant bonding of the pyrrolic part to the subjacent carbon, as schematized in Figure 9, may just move it to lower potentials. It is noted that a similar redox transition occurs in the CV of CoTPP/Vulcan HT 500 but not for the corresponding H₂TPP sample, which however is thermally less

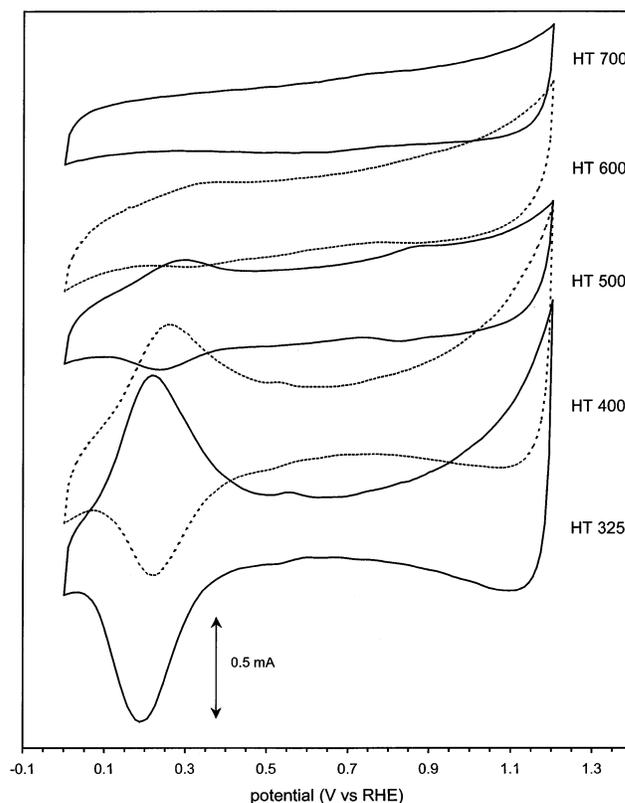


Figure 7. Cyclic voltammograms of 7 wt % FeTPP-Cl/Vulcan heat-treated at different temperatures. Leit C electrodes, argon-saturated 0.5 M H₂SO₄, 100 mV/s.

stable. By the way, Figure 9 should be taken as indicative only; we do not want to imply that all Fe-N₄ sites retain square symmetry, and indeed, we do not have any precise information on how exactly the pyrrolic fragments bind to the carbon carrier. That there is ample local variation of the precise geometry follows from the EXAFS data (vide supra).

In sum, these voltammetric data indicate that the Fe(2⁺)/Fe(3⁺) transition occurs at much lower potentials (0.2–0.4 V vs RHE) than where the oxygen reduction activity starts to be measurable (0.6–0.8 V vs RHE), which would imply that the availability of Fe(2⁺) sites at O₂ reduction potentials is extremely low. Still, on the assumption that such Fe(2⁺) sites are highly active for O₂ reduction, this shift toward higher potentials with increasing heat treatment temperature could explain the increasing activity of the FeTPP-Cl/Vulcan catalysts, in accordance with the model we proposed earlier.²⁸

In Situ Mössbauer Experiments. Three FeTPP-Cl/Vulcan samples have been studied with in situ Mössbauer spectroscopy, namely, fresh (effectively HT 325, since we are using Teflon-bonded electrodes that have been cured at 325 °C), HT 500, and HT 700. The spectra obtained, whether in the dry state, at open circuit, or under potential control, could be analyzed with four doublets (Lorentzian line shapes) in the HT 500 and HT 700 cases, but the fresh electrode resisted. It turns out that part of the iron in the fresh electrode is still characterized by relaxation phenomena like in the untreated FeTPP-Cl, precluding full analysis of these spectra. The results of all fits have been collected in Table 2. The four doublets can be qualitatively characterized as follows:

(i) Doublet I is characterized by a high isomeric shift and a high quadrupole splitting. This combination is unknown for iron porphyrins,³⁴ so we are dealing here with a yet unknown Fe(2⁺)-N₄ species, or, more likely, with an Fe(1⁺) species.

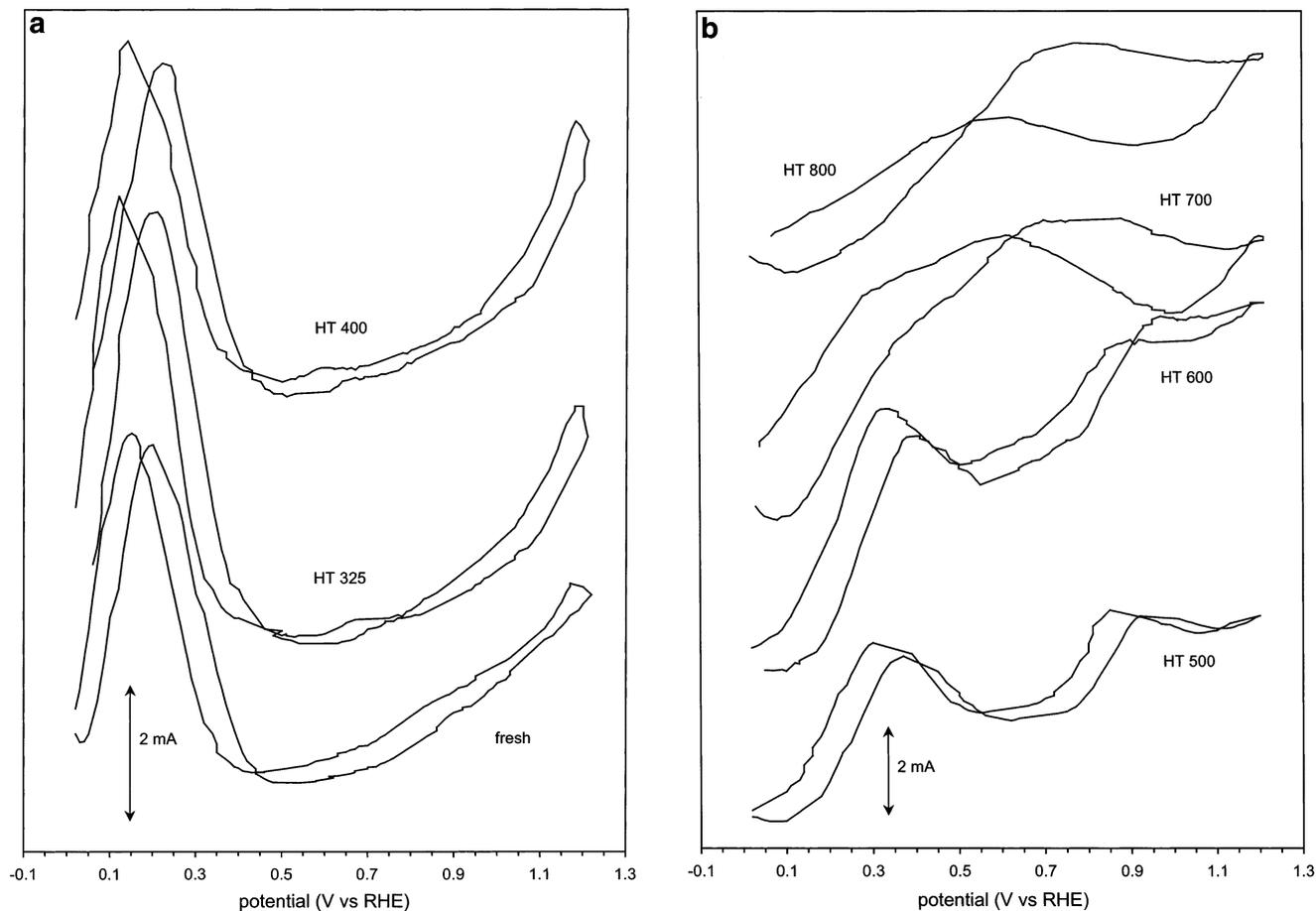


Figure 8. As in Figure 7, AC voltammetry data, Leit C electrodes, nitrogen-saturated 0.5 M H₂SO₄, 100 mV/s, 50 mV amplitude, 150 Hz.

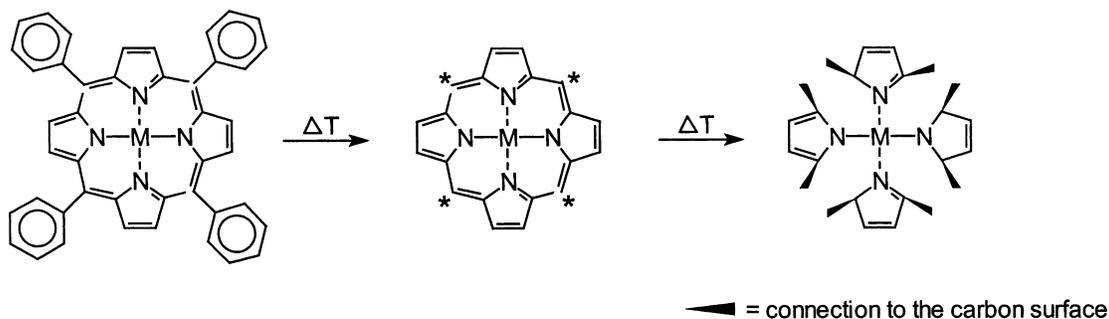


Figure 9. Visualization of the reaction of the porphyrin with the carbon during heat treatment.

(ii) Doublet II may originate from a high-spin Fe(3⁺) or a low-spin Fe(2⁺). Because the relative contribution of doublet II increases upon cathodic polarization, it is likely that it originates from an Fe(2⁺) species. Also, it has been observed for iron porphyrins that the quadrupole splitting increases when the iron moves out-of-plane,^{34,35} and such is presumably the case here (cf. the long Fe–N distance observed in EXAFS).

(iii) Doublet III is difficult to assign, since again it is not possible to discriminate between a high-spin Fe(3⁺) and a low-spin Fe(2⁺). However, on the basis of the data generally found for iron porphyrins,³⁴ a high-spin Fe(3⁺) seems most likely.

(iv) Doublet IV has a very low isomer shift, which may be indicative of Fe(4⁺).

Although definitive assignments are difficult to make, it does seem clear that the Fe species in our electrodes exist in a limited variety of reasonably well-defined electronic states. Nevertheless, the apparent coexistence of Fe(1⁺) through Fe(4⁺) species is surprising and may indicate that there are some other sites

apart from the Fe–N₄ ones. Recently, the Dodelet group has made a case for an FeN₂ site,³⁶ and although we do not have any proof of its existence in our heat-treated materials, we cannot exclude it either.

Upon comparing the Mössbauer spectra of the electrodes before and after contacting them with argon-saturated electrolyte, essentially no differences are noticed (see first three entries in Table 2 (HT 500 and HT 700), implying that at open circuit the distribution over the Fe sites is not changed to any great extent with respect to the dry catalyst. That Bae et al.⁸ came to a different conclusion is due to the fact that they studied HT 800 material, in which part of the central Fe–N₄ species is destroyed giving rise to Fe species that are soluble in the electrolyte—in which case, obviously the Mössbauer spectrum is going to be different in the dry and wet states. The present results indicate that as long as the Fe–N₄ moiety is preserved (i.e., up to HT 700) no important changes occur when contacting an FeTPP–Cl/Vulcan catalyst with acid electrolyte.

TABLE 2: Results of Lorentz Fits for Several In Situ Mössbauer Spectra^a

		δ^* (mm s ⁻¹)	Δ (mm s ⁻¹)	Γ (mm s ⁻¹)	spectr. contr. (%)
HT 500					
dry electrode 300 K	II	1.20	2.43	0.73	5
	II	0.69	1.85	0.67	15
	III	0.61	0.87	0.60	79
	IV	0.20	2.27	0.30	1
electrode in 0.5 M H ₂ SO ₄ OCP, argon 300 K	II	1.11	2.62	0.92	6
	II	0.75	1.85	0.69	15
	III	0.62	0.85	0.61	76
	IV	0.20	2.24	0.34	3
electrode in 0.5 M H ₂ SO ₄ OCP, argon 130 K	I	1.54	3.33	0.65	3
	II	0.92	2.15	0.80	20
	III	0.70	0.87	0.60	71
	IV	0.29	2.40	0.56	6
electrode in 0.5 M H ₂ SO ₄ at 0.55 V, argon 130 K	I	1.58	3.27	0.56	6
	II	0.97	2.20	0.74	21
	III	0.71	0.87	0.59	63
	IV	0.31	2.39	0.71	10
electrode in 0.5 M H ₂ SO ₄ at -0.05 V, argon 130 K	I	1.62	3.21	0.39	13
	I,II	1.24	3.37	0.42	6
	II	0.89	2.19	0.83	48
	III	0.72	0.85	0.53	33
HT 700					
dry electrode 300 K	I	1.41	3.14	0.23	2
	II	0.80	2.40	0.96	26
	III	0.63	0.96	0.64	67
	IV	0.13	2.38	0.41	5
electrode in 0.5 M H ₂ SO ₄ 300 K	I	1.36	3.03	0.28	3
	II	0.87	2.36	0.80	21
	III	0.63	0.91	0.63	63
	IV	0.20	2.45	0.84	13
electrode in 0.5 M H ₂ SO ₄ OCP, argon 130 K	I	1.61	3.17	0.31	3
	II	0.97	2.34	0.96	33
	III	0.73	0.88	0.58	50
	IV	0.20	2.40	0.68	14
electrode in 0.5 M H ₂ SO ₄ at 0.63 V, oxygen 130 K	I	1.63	3.07	0.60	6
	II	1.03	2.23	0.70	25
	III	0.73	0.82	0.56	48
	IV	0.27	2.30	0.60	21
electrode in 0.5 M H ₂ SO ₄ at -0.05 V, argon 130 K	I	1.63	3.19	0.38	16
	I,II	1.08	3.72	0.68	19
	II	1.01	2.28	0.81	43
	III	0.77	0.91	0.58	22

^a The double indication I, II means that this contribution is somehow between I and II.

To find out what fraction of the Fe sites is actually electroactive, the electrodes were polarized to -0.05 V vs RHE and cooled to 130 K, and their Mössbauer spectra were determined. In Figure 10, they are compared with the spectra obtained at the OCP, and the fit results for the HT 500 and HT 700 electrodes can be found in Table 2, last entries. An example of the deconvolution of the Mössbauer spectra into four doublets is shown in Figure 11. Clearly, a large fraction of the Fe sites is affected by the potential change—approximately two-thirds, which is similar to the result obtained by Fierro et al.²⁵ for an untreated (FeTPP)₂O/carbon electrode. Although we could not completely analyze the fresh electrode spectrum, doublet I is readily apparent in it. As to why only a relatively small part of these Fe sites show up in the CV, we can only speculate, but site heterogeneity is what comes most readily to mind (however, see below).

The Mössbauer spectra obtained at about 0.6 V vs RHE, two under oxygen and one under argon, are shown in Figure 12. The fit results for the HT 500 (under argon) and HT 700 (under

oxygen) samples are given in Table 2. It appears that there is relatively little change with respect to the OCP data, which leads us to the following remarks. (i) These Mössbauer results are consistent with our interpretation of the AC voltammetry (vide supra), since only the low-potential redox transition, which always occurs below 0.6 V, was ascribed to Fe species; in the process, the assignment of the high-potential transition to a ligand-based redox couple is strengthened. (ii) The presence of oxygen does not leave a strong imprint on the distribution of Fe over its various states, and perhaps, none should have been expected since oxygen reduction is first-order in oxygen,¹⁴ implying a low surface coverage with reaction intermediates.

Do the present in situ Mössbauer data throw any light on the question why the HT 700 sample is so much more active than the HT 500 one (cf. Figure 3)? It has been our view¹⁴ that the increased activity of heat-treated Fe-porphyrin/carbon catalysts is due to an increase of the redox potential of the central Fe ion, mainly entailing a higher number of active Fe(2⁺) sites at oxygen reduction potentials. A much-increased presence of Fe-

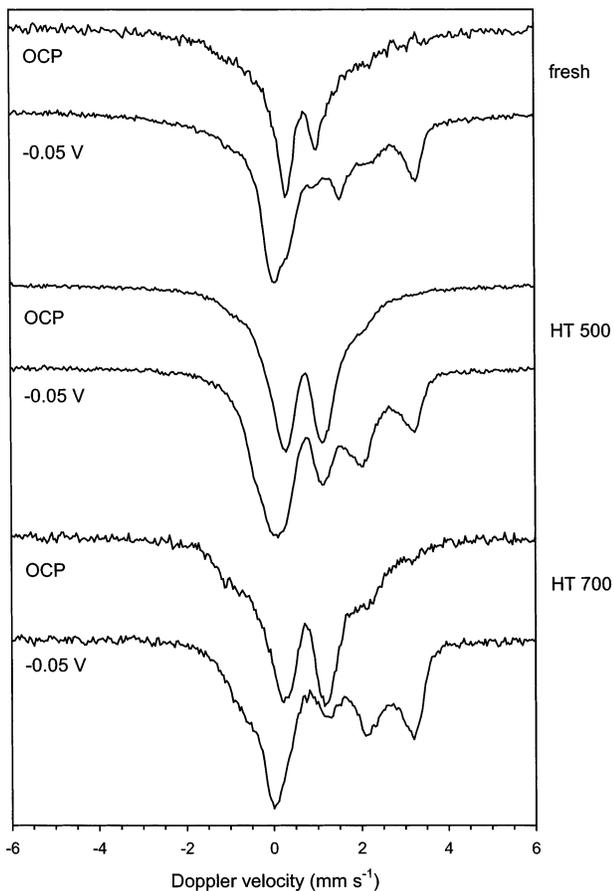


Figure 10. In situ Mössbauer spectra of fresh, HT 500, and HT 700 7 wt % $^{57}\text{FeTPP-Cl/Vulcan}$, 0.5 M H_2SO_4 , 130 K, E vs RHE.

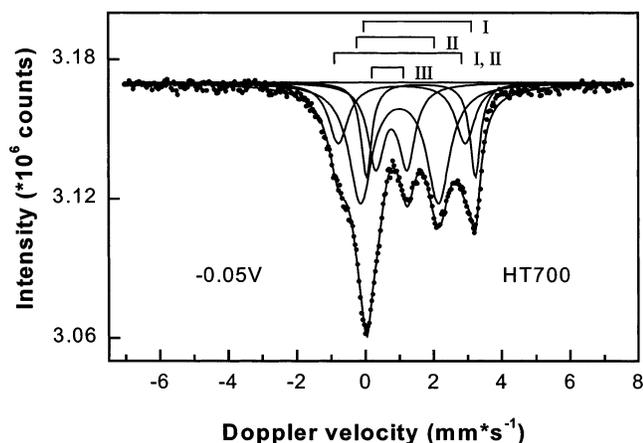


Figure 11. Deconvolution of the in situ Mössbauer spectrum of HT 700 7 wt % $^{57}\text{FeTPP-Cl/Vulcan}$, 0.5 M H_2SO_4 , 130 K, -0.05 V vs RHE.

(2^+) sites in the HT 700 electrode is not readily apparent from the data collected in Table 2. Still, there is certainly $\text{Fe}(2^+)$ present at oxygen reduction potentials and the fraction of $\text{Fe}(2^+)$ is relatively larger for the HT 700 catalyst (compare the results for the HT 500 and HT 700 electrodes in H_2SO_4 at 300 and 130 K (at OCV)). Maybe then, after all, it is only the fraction of Fe sites visible in CV that contributes to the oxygen reduction activity, which in the present case would mean that most of the porphyrin incorporated in the electrode is wasted; this may be related to the pronounced dependency of the specific activity (mA/mg chelate) on the loading (mg chelate/g support), starting out high at very low loadings and decreasing subsequently,

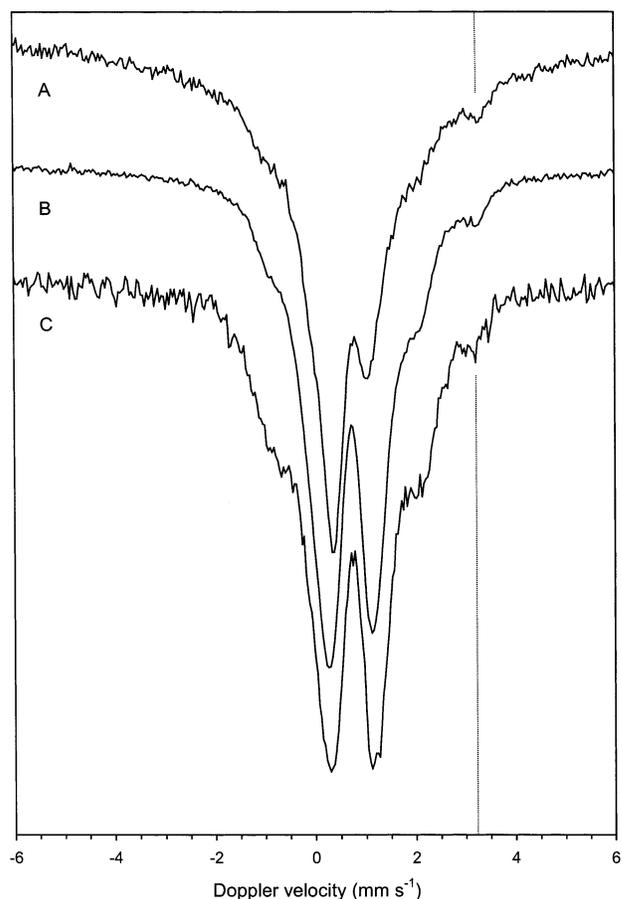


Figure 12. In situ Mössbauer spectra of fresh, HT 500, and HT 700 7 wt % $^{57}\text{FeTPP-Cl/Vulcan}$, 0.5 M H_2SO_4 , 130 K. (a) Fresh, 0.55 V vs RHE, oxygen. (b) HT 500, 0.55 V vs RHE, argon. (c) HT 700, 0.63 V vs RHE, oxygen.

which we reported for FeTPP a long time ago.¹⁴ On this interpretation, CV invisibility is connected with extremely sluggish electron transfer rates, also preventing the sites concerned from making their mark in the electrocatalysis.

Conclusions

The data presented in this paper on (heat-treated) FeTPP-Cl/Vulcan would appear to lead to the following conclusions. (I) The EXAFS results are consistent with the continued presence of the central Fe-N₄ moiety up to temperatures of 700 °C, the optimum pyrolysis temperature as far as the oxygen reduction activity is concerned, in line with our previous EXAFS study of (heat-treated) CoTPP/carbon.³ It is only at 800 °C that evidence for its partial destruction is obtained, but this leads to species that do not contribute to the O₂ reduction activity as they can be acid washed out of the catalyst without deterioration of the observed activity. (II) The CV data, combined with XPS, indicate that a heat treatment at 325 °C improves the contact between the chelate and the carbon carrier through redispersion of the initially present FeTPP-Cl crystallites. Still, only about 10% of the FeTPP-Cl applied contributes to the redox transition occurring at 0.2 V vs RHE. According to AC voltammetry, the position of this redox transition shifts to higher potentials with increasing heat treatment temperature, up to about 0.4 V vs RHE at 700 °C. After it is heated at 800 °C, however, it is no longer clearly distinguishable. (III) The in situ Mössbauer data on the (^{57}Fe -enriched) HT 500 and HT 700 samples show (i) that they are quite heterogeneous, necessitating four doublets to get a

reasonable fit; (ii) that contacting the electrode with electrolyte does not change its spectrum, indicating that the mere presence of 0.5 M H₂SO₄ does not modify the structure of the Fe sites; (iii) that polarization to low potential (−0.05 V vs RHE) does change the spectra quite considerably, and the fits, although qualitative, indicate that the majority (on the order of two-thirds) of the Fe ions has changed valence, which would imply that a lot of the Fe that is CV invisible still responds to a potential change, either because their redox potentials are distributed over a broad range or because their electron transfer kinetics are too sluggish; and (iv) that the differences observed between the HT 500 and the HT 700 electrodes at O₂ reduction potentials (about 0.6 V vs RHE) are too small to readily explain their difference in O₂ reduction activity, although the suspected active Fe(II) site is somewhat more abundant for the HT 700 material.

The picture that emerges from this is that there is no reason to abandon the redox model of O₂ electrocatalysis by TM chelates, in which the availability of Me(II)–N₄ sites at O₂ reduction potentials is an important parameter,¹² but we admittedly have a complication in the present case of Vulcan-supported FeTPP–Cl, in that only a fraction of the available Fe–N₄ sites appears to be involved in the catalysis. It is tempting to identify this fraction with what is visible in voltammetry, since it shows the shift in Fe(2⁺)/Fe(3⁺) redox potential upon pyrolysis, that is an essential feature of the redox model. We realize, however, that further work is necessary to actually prove all of this.

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References and Notes

- (1) van Veen, J. A. R.; van Baar, J. F. *Rev. Inorg. Chem.* **1982**, *4*, 293.
- (2) Ohms, D.; Gupta, S.; Tryk, D. A.; Yeager, E.; Wiesener, K. Z. *Phys. Chem. Leipzig* **1990**, *271*, 451.
- (3) van Wingerden, B.; van Veen, J. A. R.; Mensch, C. T. J. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 65.
- (4) Lalande, G.; Cote, R.; Guay, D.; Dodelet, J. P.; Weng, L. T.; Bertrand, P. *Electrochim. Acta* **1997**, *42*, 1379.
- (5) Gouerec, P.; Savy, M.; Riga, J. *Electrochim. Acta* **1998**, *43*, 743.
- (6) Gojkovic, S. L.; Gupta, S.; Savinell, R. F. *Electrochim. Acta* **1999**, *45*, 889.
- (7) Sun, G.-Q.; Wang, J.-T.; Gupta, S.; Savinell, R. F. *J. Appl. Electrochem.* **2001**, *31*, 1025.

- (8) Bae, I. T.; Tryk, D. A.; Scherson, D. A. *J. Phys. Chem. B* **1998**, *102*, 4114.
- (9) van Veen, J. A. R.; Colijn, H. A.; van Baar, J. F. *Electrochim. Acta* **1988**, *33*, 801.
- (10) Lefèvre, M.; Dodelet, J. P.; Bertrand, P. *J. Phys. Chem. B* **2000**, *104*, 11238.
- (11) Bron, M.; Fiechter, S.; Hilgendorff, M.; Bogdanoff, P. *J. Appl. Electrochem.* **2002**, *32*, 211.
- (12) Wijnoltz, A. L. Ph.D. Thesis, ISBN 90 386 0384 3, Eindhoven, 1995.
- (13) Beck, F. *J. Appl. Electrochem.* **1977**, *7*, 239.
- (14) van Veen, J. A. R.; van Baar, J. F.; Kroese, C. J.; Coolegem, J. G. F.; de Wit, N.; Colijn, H. A. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 693.
- (15) Bouwkamp-Wijnoltz, A. L.; Visscher, W.; van Veen, J. A. R. *Electrochim. Acta* **1998**, *43*, 3141.
- (16) Radyushkina, K. A.; Levina, O. A.; Tarasevich, M. R. *Elektrokhimiya* **1994**, *30*, 991.
- (17) Widelov, A.; Larsson, R. *Electrochim. Acta* **1992**, *37*, 187.
- (18) Torrens, M. A.; Straub, D. K.; Ebstein, L. M. *J. Am. Chem. Soc.* **1972**, *94*, 4160.
- (19) Torrens, M. A.; Straub, D. K.; Ebstein, L. M. *J. Am. Chem. Soc.* **1972**, *94*, 4162.
- (20) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsokoff, L. *J. Org. Chem.* **1967**, *32*, 476.
- (21) (a) Barnett, G. H.; Hudson, M. F.; Smith, K. M. *Tetrahedron Lett.* **1973**, *30*, 2887. (b) van der Made, A. W. Ph.D. Thesis, Utrecht, 1988.
- (22) Bouwkamp-Wijnoltz, A. L.; Visscher, W.; van Veen, J. A. R.; Tang, S. C. *Electrochim. Acta* **1999**, *45*, 379.
- (23) Giner, J.; Parry, J. M.; Smith, S.; Turchan, M. *J. Electrochem. Soc.* **1969**, *116*, 1692.
- (24) van den Ham, D.; Hinnen, C.; Magner, G.; Savy, M. *J. Phys. Chem.* **1987**, *91*, 4743.
- (25) Fierro, C. A.; Mohan, M.; Scherson, D. A. *Langmuir* **1990**, *6*, 1338.
- (26) Vaarkamp, M.; Linders, J. C.; Koningsberger, D. C. *Physica B* **1995**, *208/209*, 159.
- (27) (a) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992. (b) Scheidt, W. R.; Finnegan, M. *Acta Crystallogr. C* **1989**, *45*, 1214.
- (28) van Veen, J. A. R.; van Baar, J. F.; Kroese, C. J. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2827.
- (29) Maricondi, C.; Straub, D. K.; Epstein, L. M. *J. Am. Chem. Soc.* **1972**, *94*, 4157.
- (30) Blomquist, J.; Lang, H.; Larsson, R.; Widelov, A. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2007.
- (31) Scherson, D. A.; Gupta, S. L.; Fierro, C.; Yeager, E. B.; Kordesch, M. E.; Eldridge, J.; Hoffman, R. W.; Blue, J. *Electrochim. Acta* **1983**, *9*, 1205.
- (32) Ouyang, J.; Shigehara, K.; Yamada, A.; Anson, F. C. *J. Electroanal. Chem.* **1991**, *297*, 489.
- (33) Kneten Kline, K.; McDermott, M. T.; McCreery, R. L. *J. Phys. Chem.* **1994**, *98*, 5314.
- (34) Debrunner, P. G. *Phys. Bioinorg. Chem. Ser.* **1989**, *4*, 137–234.
- (35) Collman, J. P.; Gagne, R. R.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427.
- (36) Lefèvre, M.; Dodelet, J. P.; Bertrand, P. *J. Phys. Chem. B* **2002**, *106*, 8705.