*Journal of Applied Electrochemistry* **32**: 211–216, 2002.



# Catalysts for oxygen reduction from heat-treated carbon-supported iron phenantroline complexes

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Received 2 March 2001; accepted in revised form 20 November 2001

*Key words:* carbon, catalyst, iron, oxygen reduction, PEM-FC

**Abstract**

Oxygen reduction catalysts were prepared by heat treatment of carbon supported iron phenantroline complexes in Ar or $NH_3$. The optimum carbon black loading with iron was found to be 2%, the optimum heat treatment temperature was about 800 °C. X-ray diffractogramms and TEM showed the occurrence of crystalline species at higher catalyst loadings; however, these species seem not to contribute significantly to the catalytic activity. From the slope of the Koutecky–Levich plot, an average number of 3.7 electrons transferred per oxygen molecule was calculated, which is consistent with RRDE data. A Tafel slope of about 120 mV $(decade)^{-1}$ indicates that the first electron transfer is rate determining.

## 1. Introduction

Heat-treated macrocyclic transition metal complexes, such as porphyrins or phthalocyanines ('$N_4$-chelates'), with Fe and Co as the central atom have been investigated regarding their properties as oxygen reduction catalysts as well as their physico-chemical properties [e.g., 1–19]. Their enhanced stability – compared to that of nonheat-treated complexes – and their reasonable activity make them suitable alternatives for platinum as cathode catalysts in polymer electrolyte membrane fuel cells. However, long term stability of these catalysts is only observed when they are heat treated at temperatures above 700 °C [4, 6, 8–11]. It is now generally believed that the $N_4Me$ moiety, which is considered to be the active centre at lower heat-treatment temperatures (500–700 °C) [3, 6, 11, 18, 19], is largely destroyed and a new type of active centre is formed. The idea occurred that it is possible to generate such catalysts when other precursors than macrocyclic complexes are heat treated. Indeed, investigations using N-containing polymers [20–25], N-containing precursors like acetonitrile [26–29] or pyrrole and derivatives [20], or others [25] or even a carbon carrier modified with nitrogen [30], or a carbon carrier prepared during catalyst synthesis from a molecular precursor (PTCDA) [31, 32] together with transition metal salts (mainly Fe and Co) and heat treating them at temperatures above 700 °C, led to catalysts, which showed oxygen reduction at reasonably low overpotentials. Although the catalytically active centre of such catalysts is still a subject of ongoing research, it appears that it consists of a transition metal ion, which is coordinated to pyridine-type nitrogen atoms in a way which may be similar to that of the macrocyclic complex. Therefore, we tried to produce oxygen reduction catalysts using a nonmacrocyclic precursor, in which the transition metal is already coordinated to nitrogen in a pyridine-type environment. The iron phenantroline complex is such a system. Additional motivation for this investigation came from a recent study of Levèvre et al. [33], which identified via ToF-SIMS the ion $FeN_2C_4^+$ as a signature of the active centre.

This study reports electrochemical, XRD and TEM characterization of iron phenantroline complexes adsorbed onto carbon black and heat treated at temperatures above 600 °C in different atmospheres.

## 2. Experimental details

### 2.1. *Catalyst preparation*

The catalyst precursors were prepared by impregnating a commercial carbon black (Vulcan XC72, Cabot) with an aqueous solution of an iron(II)-(1,10)-phenatroline-complex ($[Fe(C_{12}H_8N_2)_3]^{2+}$, referred to in the following as $Fe(phen)_3$). Carbon black was mixed with an aqueous solution containing an appropriate amount of $Fe(phen)_3$. The amount of complex in the solution was varied in order to give catalysts with different metal loading of the carbon black. Catalysts, with metal loadings from 0.5%

to 10% related to the amount of iron and carbon black used in the synthesis, were prepared. After thorough stirring and sonicating for at least 30 min, the resulting paste was dried in an oven at 90 °C overnight. The catalyst precursor was then ground to a fine powder. The precursor was then subjected to a heat treatment step: 100 mg of the precursor were filled in a quartz tube, the closed side of which was placed in an oven, and the open end connected to either a vacuum system or to a gas supply system. The quartz tube loaded with catalyst was first evacuated and then refilled with either Ar or $NH_3$ to a pressure of 500 mbar. The oven was heated to the desired temperature (650–1000 °C, see Section 3 for details) and left for 2 h. Afterwards, the oven was removed, and the catalyst was allowed to cool in the respective atmosphere (Ar or $NH_3$). Heat-treatment steps under continuous gas flow were avoided to minimize evaporation of phenantroline, which always occurred and could be seen as a precipitate at the walls of the quartz tube. Due to this evaporation the nominal catalyst loading is related to carbon black and iron only. However, the real amount of metal in the catalyst is somewhat lower, since the precursor phenantroline also takes part in the catalyst formation. For example, the amount of metal in a catalyst heat treated in Ar, which nominally contained 1.4% Fe related to carbon black, has been determined to be 1.14% using neutron activation analysis.

### 2.2. *Electrochemical characterization*

The electrochemical characterization of the catalysts was carried out via cyclic voltammetry and rotating disc electrode (RDE) measurements. The electrodes for the RDE measurements consisted of glassy carbon rods (dia. 3 mm) which were embedded in a Teflon holder. The glassy carbon (GC) rods were covered with a mixture of the catalyst powder and Nafion® in the following way: 1 mg of catalyst was suspended in 200 $\mu$l of a 50–50 water–ethanol mixture containing 0.15% Nafion®. Twice 2.5 $\mu$l of this suspension were dropped onto the GC rod. After evaporation of the solvent and drying in an oven at 90 °C, a homogeneous, thin catalyst film formed on the electrode surface. In a series of experiments (not presented here) it has been confirmed that diffusion limitations in the electrode film can be neglected.

A one-compartment glass cell and a platinum wire counter electrode, as well as a $Hg|Hg_2SO_4|0.5$ M $H_2SO_4$ reference electrode (+0.65 V vs SHE) were used. All potentials in this paper are reported with respect to the standard hydrogen electrode.

After immersion into nitrogen-purged 0.5 M $H_2SO_4$, the electrode was exposed to cyclic voltammetry between 0 and 0.74 V for 10 min. A cyclic voltammogram (CV) was recorded. The electrolyte solution was then saturated with oxygen for 10 min while cycling the electrode between 0 and 0.74 V. A CV was recorded and subsequent the RDE-measurements were carried out.

### 2.3. *XRD and TEM measurements*

XRD analysis of the catalysts was carried out employing a Siemens diffractometer D500/5000 in Bragg–Brentano $\theta$–$2\theta$ geometry using Cu$K_\alpha$-radiation. As sample holder a (1 0 0)-oriented silicon disc was used. The diffractograms measured were identified using the JCPDS data bank.

TEM-measurements were carried out on a Philips CM 12 equipped with a super twin lens and a slow scan CCD camera. The acceleration voltage was 120 kV.

## 3. Results and discussion

Catalysts prepared with varying metal loading and heat treatment procedures were examined in RDE-experiments. Typical polarization curves for oxygen reduction at a catalyst containing 1.4% Fe can be seen in Figure 1 for several electrode rotation rates. No defined diffusion plateau is reached, however, the curves are well separated and exhibit the typical S-shape for RDE experiments. Analysis of the RDE curves was carried out using the Koutecky–Levich equation:

$$\frac{1}{j} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k} \tag{1}$$

where $B$ is the Levich constant, $\omega$ the electrode rotation rate, and $j_k$ and $j$ are kinetic current density and the total current density at a given electrode potential, respectively.

A plot of $1/j$ against $\omega^{-1/2}$ (Koutecky–Levich plot) can be used to determine the value of $B$. Figure 2 shows the Koutecky–Levich plot for the RDE curves from Figure 1 for various potentials. Parallel straight lines indicate a reaction order of one with respect to oxygen. The number of electrons transferred per oxygen molecule can be obtained from the Levich constant $B$ (Equation 1) via the following equation:

$$B = 0.2\, n F c_0 D^{2/3} v^{-1/6} \tag{2}$$

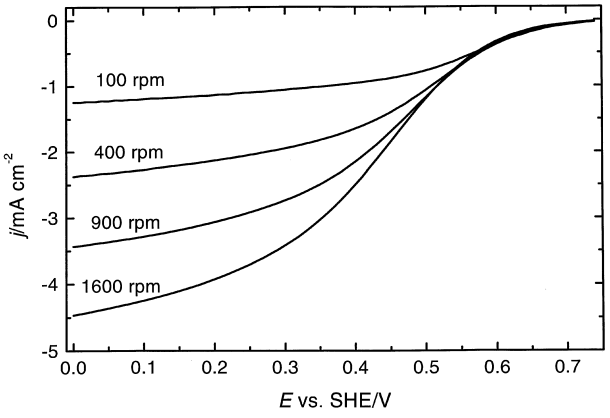


*Fig. 1.* RDE curves for oxygen reduction at a catalyst containing 1.4% Fe as $Fe(phen)_3$, supported onto carbon and heat treated in Ar at 900 °C for 2 h. Rotation rates as indicated, scan rate 5 mV $s^{-1}$. Oxygen saturated 0.5 M $H_2SO_4$.

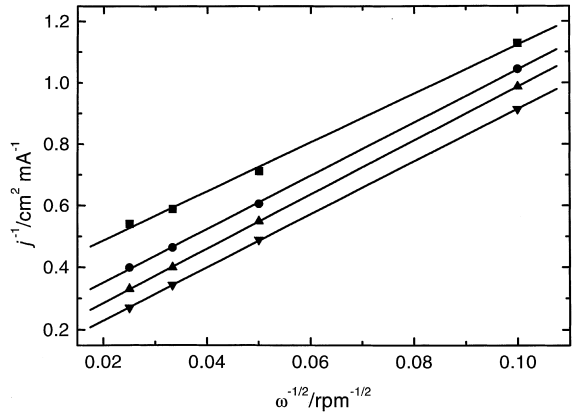


*Fig. 2.* Koutecky–Levich plots for oxygen reduction for different potentials as obtained from RDE curves of Figure 1. Key: (■) 0.45, (●) 0.40, (▲) 0.35 and (▼) 0.25 V vs SHE.

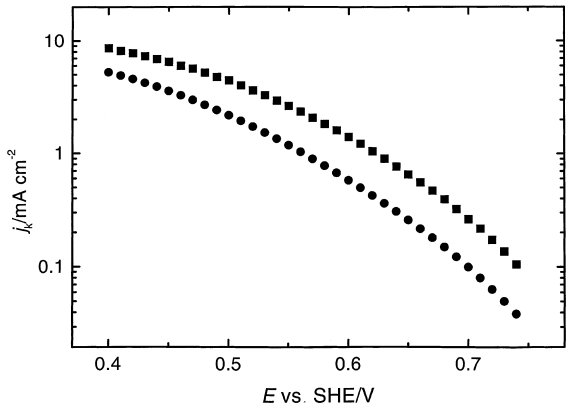


*Fig. 3.* Tafel plots for oxygen reduction at catalyst containing nominally 1.4% Fe as $Fe(phen)_3$, supported onto carbon and heat treated in different atmospheres: $NH_3$, 800 °C (■) or Ar (●), 800 °C. Data obtained from RDE measurements in oxygen saturated 0.5 M $H_2SO_4$.

where $n$ is the number of electrons, $F$(faradaic constant) = 96 486.7 C mol$^{-1}$, [34], $c_0$(bulk concentration of oxygen) = $1.13 \times 10^{-6}$ mol cm$^{-1}$ [35], $D$(diffusion coefficient for oxygen) = $1.8 \times 10^{-5}$ cm$^2$ s$^{-1}$ [35], $v$(viscosity of electrolyte) = $10.78 \times 10^{-2}$ cm$^{-2}$ s$^{-1}$ [36]. The values are given for 0.5 M $H_2SO_4$.

Using these values, a number of 3.7 electrons per oxygen molecule was calculated from the slope $1/B$ of the Koutecky–Levich plot, indicating almost complete reduction to water and a low $H_2O_2$ production during oxygen reduction. Preliminary RRDE results indicate an amount of $H_2O_2$ production of 12% at more positive potentials, decreasing to 6% at more negative potentials. This would correspond to a number of 3.76 or 3.88 electrons, respectively, under the simplified assumption of a parallel reaction of oxygen to water or hydrogen peroxide. Bouwkamps–Wijnoltz et al. [17] concluded from a detailed RRDE study on heat-treated FeTTP–Cl, that a four-electron process at more positive and a two-electron reduction at more negative potentials occurs, whereas the last one is overcompensated by a high rate of $H_2O_2$ reduction. The same may apply in the case of this catalyst, leading to the mentioned decreases of $H_2O_2$ production. Preliminary experiments on $H_2O_2$ reduction at a 1.4% $Fe(phen)_3$/V catalyst heat treated at 900 °C in Ar indeed showed a high rate of $H_2O_2$ reduction at more negative potentials.

The determination of $B$ from the slope of the Levich–Koutecky plot, as explained above, in turn allows calculation of the kinetic current $j_k$, which then can be displayed in semi-logarithmic plots against the potential $E$, the so called Tafel plots.

Figure 3 shows Tafel plots of the catalytic activity for oxygen reduction for a catalyst containing 1.4% Fe. It can be seen that the catalytic activity of a $Fe(phen)_3$/V catalyst heat treated in $NH_3$ (■) is essentially higher than the one of the same catalyst heat treated in Ar (●). Comparing the experiments of heat treatment in Ar and $NH_3$, respectively, it appears, that the nitrogen, which is necessary for the formation of the active part of the catalyst [26], mainly comes from $NH_3$. However, comparison of experiments of $Fe(phen)_3$ with results of experiments not presented here, in which carbon supported precursors from $FeSO_4$, $Fe(CN)_6^{4-}$ or from iron bipyridyl complexes were heat treated in Ar, strongly indicate, that the use of phenantroline complex as precursor enhances the activity of the catalyst, indicating that phenantroline takes part in the formation of the active centre.

Reference trials using a carbon black impregnated with phenantroline without iron clearly indicated, that the observed activity towards oxygen reduction is due to the heat treated $Fe(phen)_3$-complex and not due to either part of it.

To determine the optimum iron loading, catalysts with different loadings were prepared and heat treated in argon atmosphere at 900 °C. The results are displayed in Figure 4, where the kinetic current density at 0.6 V vs SHE (as a measure for oxygen reduction activity), taken from RDE experiments, is given as a function of catalyst loading. It can be seen that an optimum in activity is reached when the catalyst contains nominally about 2 wt% iron. At higher loadings, the activity decreases. This may be due to the formation of crystalline particles (see below), which do not contribute to the oxygen

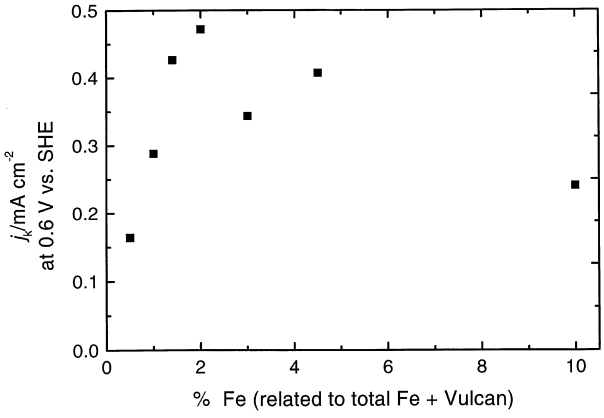


*Fig. 4.* Dependence of the oxygen reduction activity from the metal loading of the catalyst. Activity given as kinetic current density at 0.6 V vs SHE, as obtained from RDE measurements. All catalysts heat treated in Ar at 900 °C for 2 h.

reduction activity [26, 27]. In other publications on similar catalysts, optimum iron loadings have been found to be much lower (below 1%; e.g., [30, 32]). However, the optimum value for iron loading also seems to depend on the precursor used in the preparation of the catalyst [33]. Using Cl–FeTMPP, Lefèvre et al. also found 2% to be the optimum value [33]. The differences have been attributed to different degree of dispersion of the catalyst precursor. In fuel cell-tests, these catalysts showed a better performance than those prepared from iron acetate, probably indicating the formation of a higher number of active sites. A better precursor distribution therefore should enhance the optimum amount of iron and enhance catalytic activity.

Formation of crystalline particles at higher metal loadings is also evidenced by XRD and TEM. Figure 5 shows X-ray diffractogramms of catalysts heat treated in Ar at 900 °C. Broad lines with maxima at $2\theta = 25°$ and 44° were observed, which are attributed to diffraction signals of the supporting carbon, the signal at $2\theta = 33.1°$ is due to the sample holder. However, the line at $2\theta = 44°$ is superimposed by another more narrow line. This line can be attributed to α-Fe and/or iron–carbon species $Fe_xC_y$ ('martensite'). The other lines in Figure 5, together with the one at $2\theta = 44°$, can be attributed to $Fe_{1-x}S$ ('pyrrothite'). This species obviously forms via reduction of sulfate, which is present in the catalyst as anion of the precurser salt.

The increase in signals of crystalline particles seen in Figure 5 with decrease of activity found in this study supports the view that these particles do not contribute significantly to the catalytic activity. TEM images also show the occurrence of crystalline particles. In Figure 6, such a particle can be seen. It seems to be surrounded by a layer of graphitic-type carbon. The formation of crystalline particles mostly encapsulated by graphitic carbon has also been found in other studies on similar catalysts [26, 27]. These particles do not contribute to the catalytic activity.

In another series of experiments, the optimum heat treatment temperature has been identified. In Figure 7,

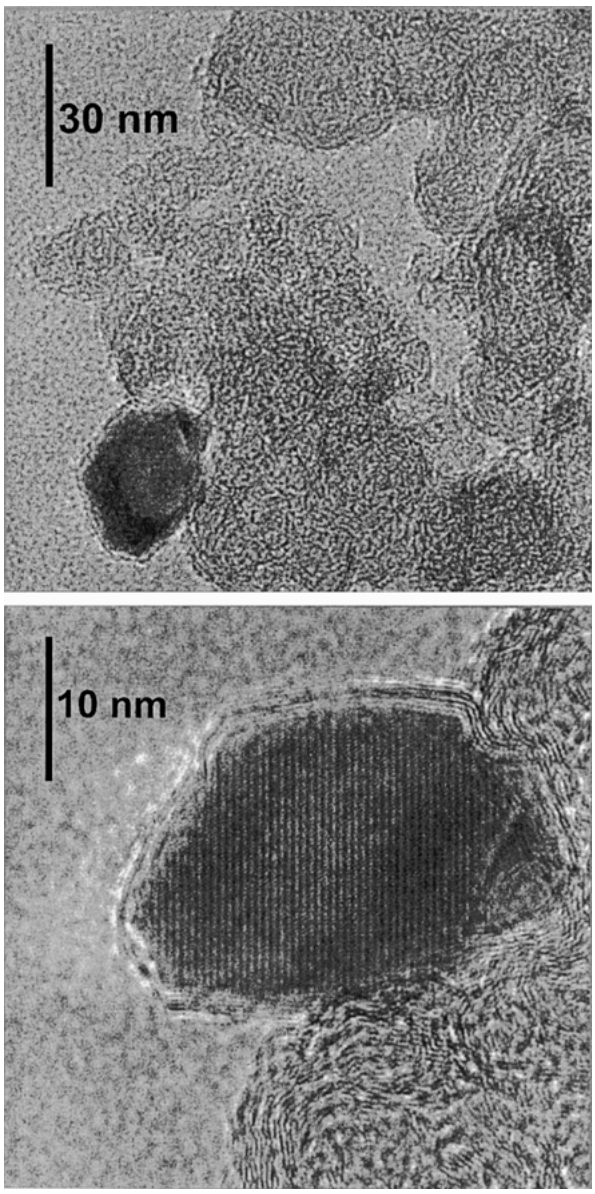


*Fig. 6.* TEM images of a catalyst containing 1% Fe from $Fe(phen)_3$, heat treated in Ar at 900 °C for 2 h.

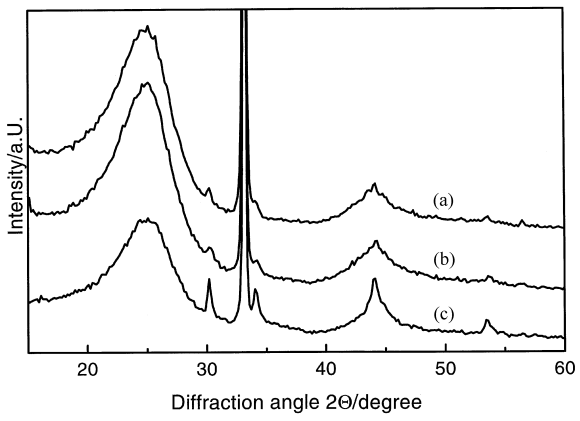


*Fig. 5.* X-ray diffractogramms for catalysts with different iron loadings, as indicated. All catalysts heat treated in Ar at 900 °C for 2 h. Key: (a) 1.4% Fe, (b) 3.0% Fe and (c) 10.0% Fe.

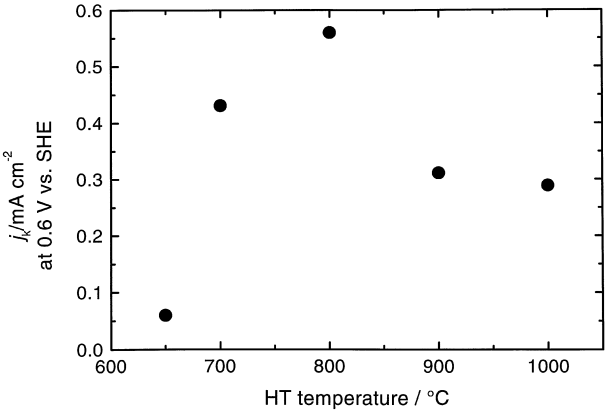


*Fig. 7.* Dependence of the oxygen reduction activity from the heat treatment temperature for catalysts heat treated in Ar. Activity given as kinetic current density at 0.6 V vs SHE, as obtained from RDE measurements in oxygen saturated 0.5 M $H_2SO_4$.

*Table 1.* Peak potentials ($E_P$), overvoltages ($\eta$), kinetic currents ($j_k$) and Tafel slopes ($\alpha$) of selected catalysts

| Catalyst loading /% | Heat treatment /°C | $\alpha$ /mV dec$^{-1}$ | $\eta$ vs 1.229 V /mV | $j_k$ at 0.6 V vs SHE /mA cm$^{-2}$ | Peak potential, $E_p$ /V vs SHE |
|---|---|---|---|---|---|
| 1 | Ar 900 | 117.7 | 450 | 0.287 | 395 |
| 2 | Ar 900 | 117.0 | 417 | 0.472 | 450 |
| 1 | $NH_3$ 700 | 121.0 | 423 | 0.431 | 460 |
| 1 | $NH_3$ 800 | 119.0 | 405 | 0.56 | 500 |
| 2 | $NH_3$ 800 | 109.9 | 398 | 1.22 | 480 |

catalytic activities of a catalyst containing 1% Fe, heat treated in $NH_3$ at different temperatures, are given as current densities at 0.6 V vs SHE. An optimum heat treatment temperature of about 800 °C is found. Using Ar atmosphere in the heat treatment step, the optimum activity is somewhat higher. Similar values have been found in other studies [33]. The differences between Ar and $NH_3$ may be explained by the reaction of $NH_3$ with the supporting carbon. This reaction can contribute to the formation of active centres, on the other hand, when the temperature is too high, etching of carbon also occurs, which may lead to the distortion of active parts.

Peak potentials ($E_P$), overvoltages ($\eta$), kinetic currents ($j_k$) and Tafel slopes ($\alpha$) of selected catalysts are summarized in Table 1. Peak potentials have been obtained via cyclic voltammetry using the same experimental conditions as for the RDE measurements but a scan rate of 50 mV s$^{-1}$. As can be seen from Figure 3, no extended linear region can be found in the Tafel plots. Therefore, the slope has been estimated in the region of the beginning oxygen reduction, that is, at 0.74 to 0.64 V (Figure 1). The variations in $\alpha$ may be explained by traces of $Fe^{2+/3+}$, which are still present in the catalyst and overlap with the oxygen reduction current; however, a value of about 120 mV (decade)$^{-1}$ is generally attributed to a first electron transfer as rate determining step. The Tafel slope is nearly independent of the heat treatment temperature and the atmosphere employed; however, the overvoltages are generally lower when using $NH_3$.

No conclusion can be drawn from the data presented about the structure of the active centre. According to the literature, it consists of iron centres within a carbon–nitrogen network. Such centres must be capable of providing four electrons for a four-electron reduction of oxygen to water, as suggested by the low $H_2O_2$ formation. Direct four-electron reduction would require the formation of clusters, which may act as electron reservoirs, or delocalized $\pi$-electron systems, which are able of delivering necessary electrons on the timescale of the experiment. However, as suggested by the preliminary RRDE data, it may be that we are dealing with a double two-electron reduction.

From the kinetic current densities at 0.6 V, it can be seen that the most active catalyst in this study was a 2% $Fe(phen)_3$/V catalyst heat treated in 800 °C in $NH_3$. The activity of these catalysts is lower than that of heat treated macrocyclic transition metal complexes but higher than that of heat treated nitrogen-containing polymers with transition metals, which are also under investigation in our laboratories. However, preliminary results indicate that improvement of the catalyst is possible. The use of a different carbon support, as well as a more sophisticated catalyst preparation and heat treatment procedure, will be investigated in the near future.

## 4. Conclusion

Oxygen reduction catalysts can be obtained on the basis of heat-treated, carbon-supported iron phenantroline complexes. An optimum value for the metal loading of about 2% has been found. The optimum heat treatment temperature depends on the atmosphere in which the catalyst is heat treated and is about 800 °C in $NH_3$. A Tafel slope of about 120 mV (decade)$^{-1}$ at lower overvoltages indicates that the first electron transfer during oxygen reduction is rate determininig. The $H_2O_2$ production of the catalysts is low. The activity of the catalysts is still inferior to that of heat treated macrocyclic transition metal complexes but further improvement may be possible.

## Acknowledgements

The help of U. Bloeck and M. Giersig from HMI Berlin, in performing TEM measurements, is gratefully acknowledged. Financial support was obtained by the BMBF under contract 0327067 B.

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