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Electrochemical reduction of oxygen: an alternative method to prepare active CoN_4 catalysts

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Abstract

An alternative method for preparing active catalysts for oxygen reduction with similar a performance as heat treated cobalt porphyrin on carbon is presented. The catalysts were prepared from cobalt acetate, carbon black and a nitrogen donor. Several nitrogen donors were investigated. The best results were obtained with 2,5-dimethylpyrrole. In this case the activity of the heat treated cobalt porphyrin could be matched. EXAFS indicated that similar active sites were found on both types of catalyst, although in the alternative catalyst some metallic cobalt is also present.

Keywords: Oxygen reduction; Electrocatalysis; Cobalt catalyst; Floating electrode; Pyrolysis

1. Introduction

When a carbon supported transition metal N_4-chelate is heat treated at 500–700°C in an inert atmosphere, its performance in the electrochemical oxygen reduction is greatly enhanced. The active sites responsible for this performance result from a reaction of the chelate with the subjacent carbon, conserving only the central MeN_4 moiety [1–4], the so-called MeN_4 supersites. That is, one synthesizes a transition metal chelate and adsorbs it onto a carbon support only to (partly) decompose it again during the heat treatment. One wonders, therefore, whether it would be possible to generate the desired MeN_4 sites in a single step simply by combining the basic components, viz. a transition metal salt, a nitrogen donor and a carbon support, and pyrolyzing the resulting mixture. If successful, this alternative preparation method would provide a cheap and easy route to active catalysts.

A first step along these lines that has often been described in the literature is the in situ synthesis of the chelate on the carbon support. For instance, FePc can be in situ synthesized in the presence of a carbon support [5–8], although different dimers and higher polymers are formed [9,10], especially if 1,2,4,5-tetracyanobenzene is used as the starting material. The use of dicyanonaphthalene and Fe(II)acetylacetonate resulted in monomeric, supported Fe–naphthalocyanine (FeNPc) [11]. All these syntheses are performed at moderate temperatures (~ 300°C). A heat treatment is performed after the synthesis. The resulting catalysts can therefore be confidently assumed to be very similar to the traditional heat treated materials.

This similarity is less evident when completely different nitrogen donors are used. Yeager and co-workers

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found that nitrogen-containing polymers can produce an active catalyst after pyrolysis [12]. After heat treatment of a mixture of polyacrylonitril (PAN), transition metal salt and carbon, a catalyst was obtained with an activity comparable to that of the heat treated metalchelates. The selectivity of the so-prepared catalysts was better than the corresponding metalchelates. Also, carbon supported polypyrrole layers, impregnated with a transition metal salt solution, gave active electrode materials after heat treatment [13,14]. These experiments appear to show that only a metal salt, a nitrogen donor and a carbon support are required to prepare active catalysts.

In this paper, we report on our evaluation of such an alternative preparation method, involving mainly pyrrole derivatives as nitrogen donors. Several nitrogen donors were investigated. The only metal salt that has been used is cobalt acetate; cobalt has been chosen for easy experimentation. Since the activity of the catalyst was particularly relevant here and cobalt catalysts are usually found to catalyse the oxygen reduction solely to hydrogen peroxide, only floating electrode measurements have been performed. This technique uses small gas-diffusion electrodes in horizontal position floating on the electrolyte surface and yields quantitative information on the intrinsic activity of the different catalysts [15,16].

The Co-loading was chosen 2–5 times higher than that of the reference CoTPP–catalyst (H_2TPP = meso-tetraphenylporphyrin) with the idea that in constructing the (CoN_4) active sites from Co^{2+} and pyrrole you need much less space than when starting from a tetraphenylporphyrin, so that a higher site density should be possible. To check whether in fact MeN_4-moieties were formed EXAFS-measurements were performed, in which the most active 'alternative' catalyst was compared with a pyrolysed Co–porphyrin on carbon black.

2. Experimental

2.1. Nitrogendonors

A series of monomer nitrogen donors was used. *N*-methylpyrrole (m.p. −57°C, b.p. 130°C), 2,5-dimethylpyrrole (b.p. 170–2°C), 2,5-dimethyl-3-pyrrolin (b.p. 102–105°C), maleimid (m.p. 92–94°C) and imidazole (m.p. 90–1°C, b.p. 257°C) were obtained from Janssen Chimica and used as received. The other monomers were prepared as described below.

2.1.1. Pyrrole

Freshly distilled pyrrole was used. m.p. −23°C, b.p. 130°C.

2.1.2. 3-Carboethoxy-4-methylpyrrole [17]

A solution of 3.6 g (30 mmol) ethylcrotonate and 5.9 g (30 mmol) *p*-toluene-sulfonylmethylisocyanide in 15 ml DMSO and 30 ml water was slowly added under nitrogen to a solution of 2 g NaH in 20 ml ether. When the gas evolution stopped some more DMSO was added. The reaction mixture was stirred for 90 min. A total of 50 ml water was added. The reaction mixture was twice extracted with ether. The combined ether extracts were washed with an aqueous solution of NaCl. The ether solution was dried and the ether was evaporated. 3-Carboethoxy-4-methylpyrrole was purified with a small amount of hexane and dried. Yield 2.95 g (64%). The purity was checked with GLC and ^1H NMR. M.p. 69–71°C.

2.1.3. 3,4-Dimethylpyrrole [17]

A solution of 5 g 3-carboethoxy-4-methyl-pyrrole in 50 ml benzene was added slowly added to a benzene solution of 23 g 2-methoxyethoxy aluminate at room temperature (r.t.) under nitrogen atmosphere. The reaction mixture was stirred for 4 h. In total a 100 ml water was slowly added. The benzene-layer was separated, twice extracted with 200 ml water and dried. The solvent was evaporated. Yield 1.4 g (44%). The purity was checked with GLC and ^1H NMR. B.p. 65°C (14 mmHg).

2.1.4. 2,5-Diphenylpyrrole

2,5-Diphenylpyrrole was kindly donated by L. Groenendaal (TUE) and was prepared as described elsewhere [18]. The diphenylpyrrole contained a BOC-group to protect the nitrogen. The removal of this BOC group can generally be performed by thermal treatment in vacuum at 125°C [18], so it was assumed that this group was removed in situ during the heat treatment. M.p. 143.5°C.

Two nitrogen containing polymer donors were used: polyacrylonitrile (PAN, obtained from Janssen Chimica) and polypyrrole (pyrrolblack, PB). The latter was prepared as follows [19]: 4 ml freshly distilled pyrrole was added to a mixture of 200 ml acetic acid (2 M) and 100 ml 30% hydrogen peroxide. The solution was stirred for 6 h in the dark. The pyrrolblack was obtained by filtration and dried.

2.2. Catalysts

Different carbon supports have been used: a carbon black (Vulcan XC-72R, obtained from Cabot, referred to as 'Vulcan') and an active carbon (Norit BRX, obtained from Norit, referred to as 'BRX'). Vulcan is a high surface area carbon black (325 m^2 g^{-1}). The pore volume is 1.23 cm^3 g^{-1}, the average pore size was about 5 nm (no micropores, only meso- and macropores). The iron content was extremely low: 0.002 wt.%.

The reactivity of the surface was low, due to the absence of functional groups. BRX has a CO_2 surface area of about 650 m^2 g^{-1} [2] and a BET surface area of 1800 m^2 g^{-1}, this latter value is however not reliable since the BET theory can not be applied in the case of micropores. The iron content was 0.25–0.05 wt.%, the silica content 5–6 wt.%. The average particle size was 10 μm.

An oxidised Vulcan was obtained after reflux in 1 M HNO_3 (5 g l^{-1}, 5 h). After filtration the carbon was thoroughly washed with water until the washing liquid became neutral, followed by washing with 1 M KOH, water until the washing liquid became colourless, 1 M HCl and finally water until the washing liquid contained no longer any salt. The carbon was dried at 125°C. Yield 45%. The use of more concentrated nitric acid [20] resulted in very small carbon particles that remained in solution.

After this treatment Vulcan ox contained oxygen functionalities on the surface [21]. The IR spectrum showed the appearance of vibrations around 1760 cm^{-1}, indicating the presence of aromatic carboxyl and lactone groups on the surface. No information about the density of the surface groups can be given. No exact data on the density of Vulcan and Vulcan ox are available, but the impression was that the density had increased as a result of the oxidation. The surface area had decreased to 250 m^2 g^{-1}.

In most cases 1.5 wt.% Co/Vulcan was used to prepare the catalysts, prepared via the ‘incipient wetness’ technique: cobalt acetate was dissolved in a minimum amount of water, the carbon was added and the mixture was homogenized to form a paste. This paste was dried slowly: 1 h at 20°C, 1 h at 40°C etc. upto 120°C. The dried carbon was pulverized. In total 1.5 wt.% Co/Vulcan ox and 4.5 wt.% Co/BRX were prepared analogously.

The catalysts were prepared using thick-walled quartz (Carius) tubes. The cobalt containing Vulcan was brought into the tube, the nitrogen donor was added and the tube was evacuated and sealed. If the nitrogen donor was a solid, it was dissolved in a small amount of ethanol and put into the tube, after which the tube was heated to evaporate the ethanol. In the case of imidazole the synthesis was slightly different: cobalt acetate and imidazole were dissolved in ethanol, Vulcan was added and the ethanol evaporated. The thus loaded Vulcan was brought into the tube. In the case of the pyrrolblack catalyst the PB was added first: the PB was dissolved in a KOH solution and the Vulcan was added. The suspension was slowly acidified with acetic acid to assure adsorption of the polymer onto the carbon. After drying the PB containing Vulcan, the cobalt acetate was added via the ‘incipient wetness’ technique. The evacuated and sealed Carius tubes were heated as follows: 10°C per min, 2 h at 300°C, 10°C per min, 2 h at 700°C, cooling down to r.t.

Also, PAN containing catalysts were prepared according to the method of Gupta et al. who used DMF [12] as a solvent. The PAN loading was varied; at high loadings a rather glassy material was obtained, while at lower loadings the catalysts remain powdery. Finally, a catalyst was prepared following the method of Seeliger and Hamnett [14] using $K_3Co(CN)_6$ and polypyrrole. These catalysts were not pyrolysed using a Carius tube, but in a down flow reactor used for the pyrolysis of the cobalt–tetraphenylporphyrin (CoTPP) containing catalyst.

All results will be compared with the performance of 7 wt.% CoTPP/Vulcan HT 700 (heat treated at 700°C) which was considered as the standard (prepared as described in Ref. [22]). This sample contains 0.62 wt.% Co.

The catalysts used for the EXAFS measurements were acid-treated to remove any cobalt that was not chemically bound to the catalyst surface. During the acid treatment the catalyst was suspended for 10–15 min in 0.5 M H_2SO_4 at 80°C, followed by extensive rinsing with water. The acid treatment leaves the activity of the catalyst largely intact [4].

2.3. Electrochemical setup

The floating electrodes were prepared from a catalyst/teflon mixture. A total of 15 mg catalyst was ultrasonically suspended in water, a little alcohol was first applied to ensure complete wetting. The 935 μl 250 times diluted teflon suspension (Fluon GP-1 from duPont) was added and the ultrasonic treatment was prolonged for about 1 min. Thereafter, the suspension was filtered over a 0.45 μm membrane filter. The resulting paste was brought onto three gold screens (80 mesh, ϕ 15 mm) which served as current collectors. The electrodes were dried for 1 h at 125°C. Sintering of the dried electrodes was performed in argon atmosphere at 325 ± 2°C. The teflon content in the final dry electrode was 20 wt.%.

The electrochemical experiments were performed using a three-electrode cell similar as described in Ref. [16]. The disk part of a Tacussel bipotentiostat was used connected to a Wenking scan generator. A reversible hydrogen electrode was used as a reference electrode and a Pt-foil served as a counter electrode. The scan velocity was 1 mV s^{-1}. The first scans are plotted.

Before installing an electrode the electrolyte was saturated with oxygen. Electrodes with Vulcan supported catalysts were first wetted with alcohol and subsequently rinsed and saturated with water. Thereafter, the electrodes were well dried with a tissue and brought onto a Pt-ring (with connection to the potentiostat) using a teflon holding ring. The electrolyte level was adjusted so that it just contacted the electrode and the electrode was stabilized for at least 2 h.

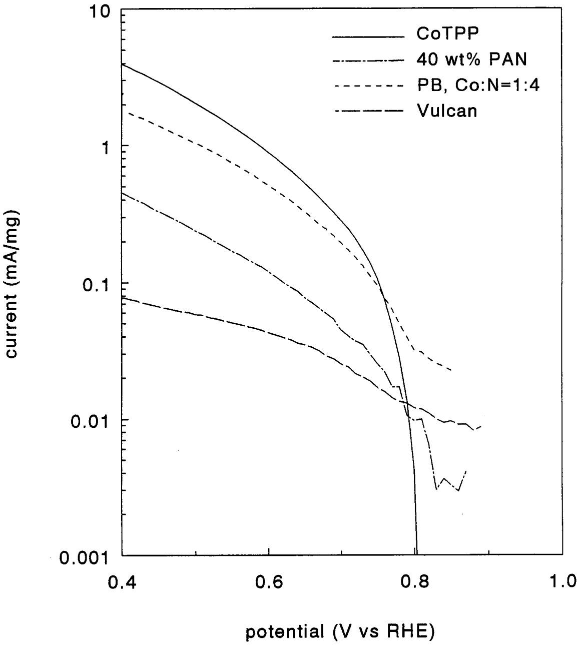

Fig. 1. Oxygen reduction activity of 1.5 wt.% Co/PAN/Vulcan 40/60 HT 700 and 1.5 wt.% Co/PB/Vulcan Co:N = 1:4 HT 700. 0.5 M H_2SO_4, 1 mV s^{-1}.

2.4. EXAFS

Room temperature EXAFS 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 cobalt, the K-edge at 7.71 keV was used. The raw data taken at Daresbury were then transferred onto a 8 mm data tape, and processed at Westhollow Technology Center. The data were reduced and analysed using the C^2.EXAFS module of the Cerius [23] module from Molecular Simulations Inc. This module is derived from the EXCURV92 program from Daresbury [23]. Samples of the catalysts were made by packing the catalysts into a 1/4-inch thick sample holder just prior to data collection.

3. Results

3.1. Electrochemical measurements

All alternative catalysts showed activity for the oxygen reduction only after heat treatment. It appeared that treatment at 700°C resulted in the highest activities. Furthermore, it was discovered that a pretreatment at 300°C was beneficial. This is ascribed to an improved distribution of the nitrogen donor throughout the sample.

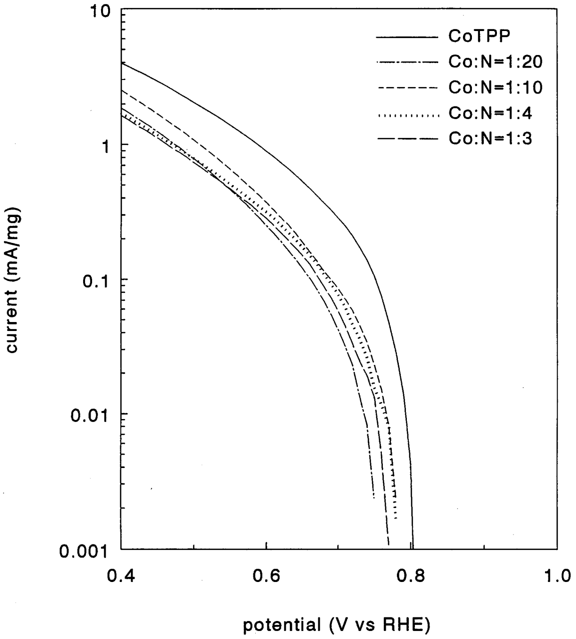

Fig. 2. Variation of nitrogen content for 1.5 wt.% Co/3,4-dimethylpyrrole/Vulcan HT 700, 0.5 M H_2SO_4, 1 mV s^{-1}.

The high activity that was claimed by Gupta et al. [12] for a catalyst containing 40 wt.% PAN could not

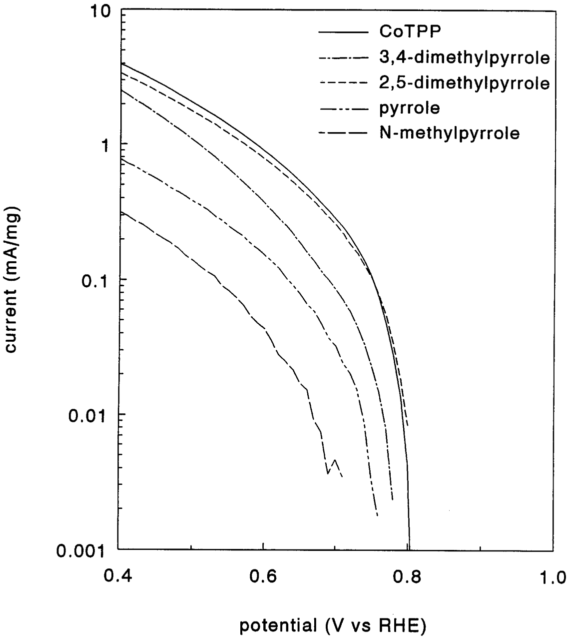

Fig. 3. Various pyrroles added as nitrogen donor in 1.5 wt.% Co/N-donor/Vulcan Co:N = 1:10 HT 700, 0.5 M H_2SO_4, 1 mV s^{-1}.

be reproduced (Fig. 1). This is in agreement with the results obtained by Dok Hi et al. [24]. Also, the high activity for the catalyst containing polypyrrole and $K_3Co(CN)_6$ claimed by Seeliger and Hamnett [14] could not be reproduced: almost no activity was observed (not shown in Fig. 1).

During the investigations with PAN catalysts, it was revealed that the activity already levels off at relatively low amounts of PAN. The PAN loading could be lowered to a Co:N atomic ratio of about 1:4–6. At still lower PAN contents the activity decreased considerably. However, the activity of the PAN catalysts was in all cases rather low.

Considerably higher activity was obtained for catalysts with a polypyrrole nitrogen donor (Fig. 1). Here again only small amounts of nitrogen were needed to prepare active catalysts. The activity of such a PB containing catalyst is close to the activity of the heat treated CoTPP reference.

For catalysts with pyrrole added as monomer, it appeared that much of the added pyrrole did not react during the heat treatment but formed ammonia in the gas phase. Addition of benzaldehyde considerably increased the activity of the heat treated catalyst, but since this was more an in situ synthesis of the tetraphenylporphyrin, this was not further investigated. To increase the thermal stability of the pyrrole, 3,4-dimethylpyrrole was used. Indeed, this increased the activity considerably (Fig. 2), although the activity of the heat treated CoTPP was not reached. A variation of the amount of nitrogen donor revealed that these variations did not have a large effect. An amount of nitrogen donor that was much more than the amount of cobalt present (e.g. Co:N = 1:20) lowers the activity. It was decided that a starting Co:N ratio of 1:10 would be best in most cases.

Fig. 3 shows a comparison between several pyrroles. The highest activity is obtained with 2,5-dimethylpyrrole. In this case, indeed, the activity of CoTPP HT 700 was matched! The activity of the *N*-methylpyrrole was very low. Fig. 4 gives the activity of several other nitrogen donors, here only in the case of the 3-carboethoxy-4-methyl-pyrrole is reasonable activity reached.

The effect of the support is given in Fig. 5 for 2,5-dimethylpyrrole. It appears that the presence of carbon surface groups results in a lower activity.

3.2. EXAFS measurements

EXAFS measurements were performed on three samples:

(i) 7 wt.% CoTPP/Vulcan
(ii) 7 wt.% CoTPP/Vulcan HT 700
(iii) 1.5 wt.% Co/2,5-dimethylpyrrole/Vulcan Co:N = 1:10 HT 700

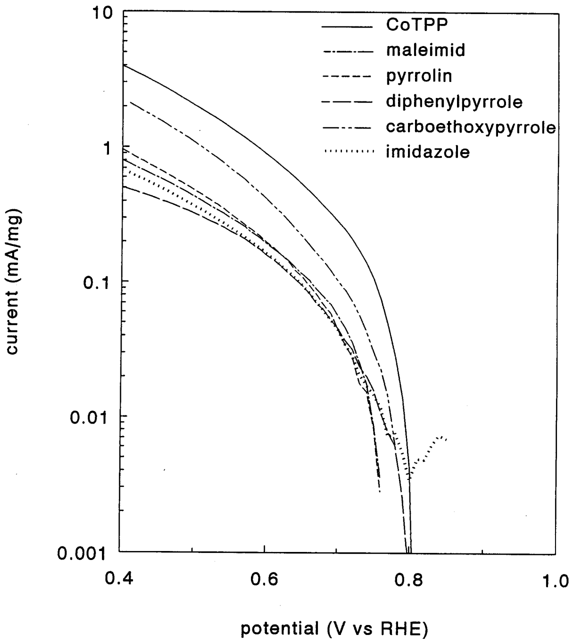

Fig. 4. Various nitrogen donors in 1.5 wt.% Co/N-donor/Vulcan Co:N = 1:10 HT 700, 0.5 M H_2SO_4, 1 mV s^{-1}.

Both heat treated samples were washed with acid to remove any cobalt that was not chemically bound to the catalyst surface.

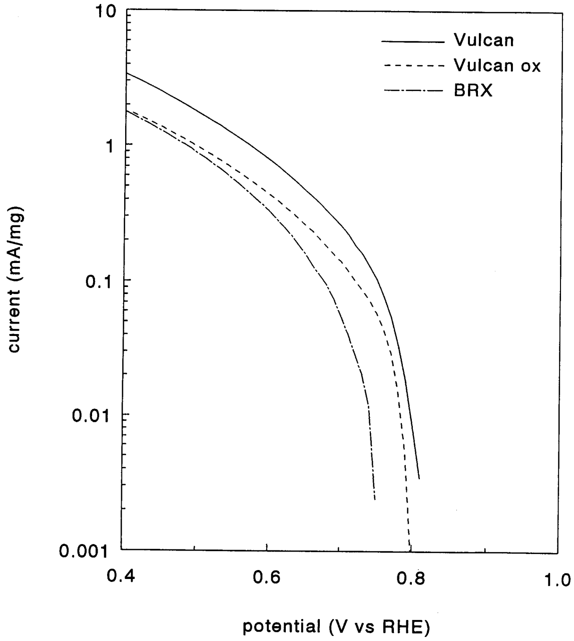

Fig. 5. Variation of support for 1.5 wt.% Co/2,5-dimethylpyrrole/Vulcan or Vulcan ox Co:N = 1:10 HT 700. (BRX 4.5 wt.% Co) 0.5 M H_2SO_4, 1 mV s^{-1}.

Table 1
Cobalt K-edge EXAFS data for three catalysts[a,b]

Catalyst	% fit	First-neighbor shell				Second-neighbor shell				Third-neighbor shell			
		A	R	W	Z	A	R	W	Z	A	R	W	Z
(i)	3.5	37.1	1.94	0.005	N	62.0	2.99	0.005	C	59.9	3.37	0.005	C
(ii)	4.1	34.3	1.90	0.010	N	32.3	2.84	0.010	C				
(iii)	4.2	18.0	1.90	0.017	N	21.8	2.48	0.020	Co	57.1	2.80	0.020	C

[a] (i) 7 wt.% CoTPP/Vulcan; (ii) 7 wt.% CoTPP/Vulcan HT 700; (iii) 1.5 wt.% Co/2,5-dimethylpyrrole/Vulcan Co:N = 1:10 HT 700.

[b] A, amplitude; R, interatomic distance (±0.02 Å), W, Debye–Waller factor (σ^2 in Å^2); Z, atom type; %fit, least-squares agreement.

The EXAFS-results are shown in Table 1. The EXAFS analysis of sample (i) was essentially identical to that found previously for the as prepared 5,10,15,20-tetra-(*p*-chlorophenyl)porphyrinatocobalt(II) supported on BRX [2]. As before, the first-neighbor shell of cobalt consisted of nitrogen atoms at 1.94 Å (versus 1.96 Å in Ref. [2]), with the second- and third-neighbor shells being carbon atoms from the porphyrin rings at 2.99 and 3.37 Å (versus 2.99 and 3.35 Å in Ref. [2]). The relative amplitudes were also in reasonably good agreement with the corresponding values found in Ref. [2] (case b). Heat treatment and acid washing of sample (i) led to a shortening of the Co–N distance to 1.90 Å, with the second shell neighbor of carbon atoms shortening to 2.84 Å. The third shell was no longer discernible. The first neighbor distance is in agreement with that found for Ref. [2] (case e, 1.88 Å), while the second neighbor distance is somewhat lower than what was found in Ref. [2] (2.95 Å). As expected, the first and second shells amplitudes both decreased from the corresponding values of sample (i), and an increase in the Debye–Waller factor points to an increase in disorder.

The EXAFS of sample (iii) is similar to that of sample (ii) except for the presence of a Co–Co signal at 2.48 Å (Co metal, 2.46 Å). Again, we have a first-shell of nitrogen atoms at 1.90 Å, then a second shell of carbon atoms at 2.80 Å. The amplitudes of sample (iii) are not meaningfully comparable to those in sample (ii) due to the severe peak overlap, the presence of the Co metal, and the inequality of the Debeye–Waller factors.

4. Discussion

Catalysts based on PAN can be prepared that are active in oxygen reduction. However, the activity is much lower than that observed for heat treated CoTPP/Vulcan. This is in contrast with the results of Gupta et al. [12], who found comparable activities. The activity of the PAN catalyst may partly be explained by assuming that heat treated PAN has some activity in oxygen reduction and hydrogen peroxide decomposition [25], which might also account for the high selectivity observed by Gupta et al. [12].

The fact that higher activity is observed if (substituted) pyrroles are used, instead of other nitrogen donors, already points to a possible similarity between the active site that is formed during the synthesis of the alternative catalyst and the active site of a heat treated metalchelate. The EXAFS data are consistent with the idea that in the case of the alternative catalysts the active site is essentially the same as the one found for the heat treated cobalt porphyrins (see below).

For iron-containing polypyrrole it was found with EXAFS that the iron is surrounded by four pyrrole-nitrogens in a structure that approximates a porphyrin surrounding [26]. Strong Fe–N interaction was also observed with Mössbauer spectroscopy [27]. This indicates that a four-fold coordination of nitrogen towards a metal ion is favourable and can be formed rather easily.

The heat treated alternative catalyst contained a residual amount of cobalt metal that was not completely removed by the acid treatment. This metallic cobalt could not be observed when the catalysts were studied with TEM (transmission electron microscopy), so the particles should be extremely small. The possible role of these small, presumably encapsulated, metallic particles in the reduction of oxygen can only be speculated, but the most recent evidence points to their not being (part of) the active site [1d].

The fact that the optimum Co:N preparation ratio is not exactly found at 4 does not imply that the ratio in the active site is not 4. It is likely that some nitrogen donors undergo other reactions (e.g. in the gas phase or with carbon surface groups) leading to lower nitrogen utilization.What happens at very high N-contents (Co:N = 1:20) we do not know; it might be that reactions between pyrrole and the carbon support modify the latter such that the tendency of Co-ions to form CoN_4 structures is compromised, or perhaps the pyrrole molecules start to react with each other to such an extent that Co–N active site formation suffers.

Moreover, not all the cobalt present forms an active site: the initial amount of cobalt is about three times the amount that is present in the fresh CoTPP catalyst, indicating that a large fraction of cobalt and nitrogen donor is 'lost' during the synthesis. The maximum 'yield' of active sites, based on Co, is an order of 40% (i.e. when using 2,5-dimethylpyrrole, assuming (i) no loss of sites in CoTPP/Vulcan HT 700, and (ii) the active sites of the CoTPP and pyrrole-based catalysts being identical); this may be compared to the 23% yield of H_2TPP when using benzaldehyde and pyrrole, but no Co [28].

Comparison of the activity of the different pyrroles catalysts shows that the thermal stability of the nitrogen donor is of importance. The low activity of the catalyst prepared from *N*-methylpyrrole might be explained by its low boiling point. Another possibility is that here the nitrogen is 'protected' and can not coordinate towards the metal ion. However, this methyl-group is thermally labile so it will easily be removed [29]. This removal is also the first step in the thermal destruction of the *N*-methylpyrrole. Both possibilities will impede the CoN_4 formation and thus result in low activity in the oxygen reduction reaction.

The high activity of the 2,5-dimethylpyrrole catalyst is remarkable. For polypyrroles it was found [29] that the polymerization takes place via the 2 and 5 position which are also the connecting atoms in the porphyrin-ring. One would therefore perhaps not have expected that the 2,5-dimethylpyrrole gives such a high activity. However, the high activity can be explained by assuming that the methyl groups are reasonably thermally labile. This might also explain the observed activity difference between the 2,5- and 3,4-dimethylpyrrol, since the latter is expected to be even less stable due to the electron distribution in the molecule. Upon removal of the methyl group pyridine structures can be formed [29], thus leading to lower utilization of the added pyrrole.

It appears that nitrogen donors that are more saturated, such as 2,5-dimethyl-3-pyrrolin and maleïmid, give a lower activity. The low activity of the imidazol was somewhat surprising, since this molecule is expected to coordinate towards metal ions in solution, thus providing a better starting point for the synthesis. If the activity of 3-carboethoxy-4-methyl-pyrrole and 2,5-diphenylpyrrole are compared, one should expect the diphenylpyrrole to be more thermally stable and thus show a higher activity. This is not observed. It is possible that the protecting BOC-group is not removed. Another, more likely possibility is that the diphenylpyrrole is too thermally stable: other reactions involving the metal ion may already occur, which leaves less free cobalt ions to react with the N-donor forming an active site.

The differences in activity between the different supports point to the necessity of excluding side-reactions like the reaction of the cobalt or the nitrogen donor with the support. The cobalt ions can efficiently react with the nitrogen donors to form active sites only if no surface groups are present (in contrast, Gouérec et al. [30] report that when pyrolyzing CoTAA/C it is advantageous to have surface groups there). Besides the side-reactions mentioned, it is also possible that in the case of active carbon the nitrogen donors are too strongly adsorbed onto the carbon surface (in the pores) such that reaction of the cobalt ions with the carbon surface groups already occurs when the nitrogen donor is still strongly adsorbed.

5. Conclusions

It was shown that it is possible to prepare catalysts that are active in oxygen reduction by pyrolysis of a mixture of a metal salt, a nitrogen donor and a carbon support. It appears that only small, almost stoichiometric amounts of nitrogen donors are needed to obtain active catalysts. The choice of the nitrogen donor is of importance for the resulting activity. The best catalysts were prepared with 2,5-dimethyl-pyrrole that gave the same result as 7 wt.% CoTPP/Vulcan HT 700, and polypyrrole, that came close to this activity.

The best results were obtained when reasonably thermally stable, but not too stable nitrogen donors were used, since a certain mobility and/or reactivity is required. It appears that (substituted) pyrroles yield the most active catalysts. This points to a similarity with the pyrolysed metal chelates. To optimize the metal and nitrogen donor utilization, side-reactions have to be prevented and the absence of carbon surface groups certainly is an advantage.

EXAFS data clearly show that the active site that is formed by reaction of the metal salt, nitrogen donor and carbon support is essentially the same as the site formed during heat treatment of a cobalt porphyrin on carbon. In both cases a so called CoN_4 supersite is very likely being formed.

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