

Oxygen reduction catalysed by carbon supported iridium-chelates

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OXYGEN REDUCTION CATALYSED BY CARBON SUPPORTED IRIIDIUM-CHELATES

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Abstract—Carbon supported iridium-octaethylporphyrin (IrOEP), iridium-tetraphenylporphyrin (IrTPP) and iridium-phthalocyanine (IrPc) were studied in acid for the oxygen reduction. Both porphyrins give a four-electron reduction, although a peculiar deactivation at low potentials occurs. At IrPc and heat treated porphyrins hydrogen peroxide is formed. Results are compared with carbon monoxide oxidation experiments at these catalysts. A single site mechanism is proposed for the oxygen reduction mechanism.

Key words: oxygen reduction, iridium-octaethylporphyrin, iridium-tetraphenylporphyrin, iridium-phthalocyanine, pyrolysis.

1. INTRODUCTION

Carbon supported transition metal complexes with N_4 -ligands are frequently studied as oxygen reduction catalysts for acid-electrolyte fuel cells[1]. The selectivity to water of most supported metal chelates, especially in acid media, is poor[2]. Iridium-octaethylporphyrin (IrOEP) is the only known mono-metal-chelate that catalyses the direct four-electron reduction[3] in acid; iridium-tetraphenylporphyrin (IrTPP) however does not reveal any activity[3, 4]. It has been established that for many chelates pyrolysis in inert atmosphere increases the activity and improves the stability[5, 6]. After heat treatment, supported IrTPP and IrOEP appear to be the most active among the transition metal chelates[7]; data on the selectivity of these catalysts are not available. High selectivity is often supposed to be related with a dual site mechanism[3, 8, 9]. However, also a mono-metal-site can form an activated complex for oxygen-oxygen bond cleavage[10, 11].

CO oxidation experiments can help to get more insight to distinguish between a single or dual site mechanism, since it has been realized earlier[12, 13] that this oxidation proceeds via a single site mechanism. CO is oxidized in the same potential region in which the oxygen reduction takes place. Therefore CO oxidation behaviour could throw light on the oxygen reduction mechanism.

In the present study of O_2 reduction at Ir-chelates (irreversibly adsorbed and carbon-supported catalysts) is studied with the rotating ring-disc technique and the floating electrode system. The results are compared with carbon monoxide oxidation experiments.

2. EXPERIMENTAL

All chemicals were of analytical grade and used as received, unless otherwise stated.

2.1. Porphyrins

Octaethylporphyrin (H_2OEP) was purchased from Strem Chemicals. The tetraphenylporphyrin (H_2TPP) was prepared using the Adler-method[14]. Metallation of the free-base porphyrins was performed using a method adapted from Ogoshi *et al.*[15]. The iridium-complex used for metallation, di- μ -chloro-bis(1,5-cyclooctadiene)di-iridium(I), was prepared according to the method described by Herde *et al.*[16].

100 mg H_2TPP and a stoichiometric amount of the iridium-complex were dissolved in 30 ml decaline. The reaction mixture was refluxed for 5 h under nitrogen. The reaction was followed spectrophotometrically. The solvent was distilled off under vacuum. Recrystallization could sometimes be performed using CH_2Cl_2 /ethanol or CH_2Cl_2 /hexane. Otherwise the product was twice dissolved in CH_2Cl_2 , the solution was filtered and brought to dryness. Drying of the product at 90°C and 0.1 mbar yielded 123 mg IrTPP (90%). IrOEP was prepared in the same way. The axial ligands are supposed to be a chloride and a carbonyl, the latter originating from the cyclooctadiene[15]. The assumption of the existence of this ligand is based upon the peak in the infrared spectrum at 2050 and 2054 cm^{-1} (IrOEP and IrTPP, respectively). *Uv-Vis* and *ir* spectra of the iridium-porphyrins were in accordance with data of Ogoshi *et al.*[15]. The porphyrins were not stable towards prolonged exposure to air and were stored under nitrogen.

2.2. Phthalocyanine

Iridium-phthalocyanine-chloride (IrPc-Cl) was prepared using a combination of published[17–19]. 857 mg (6.7 mmol) *o*-dicyanobenzene was dissolved in 5 ml dry 1-chloronaphthalene of about 150°C. 500 mg (1.7 mmol) iridium(III) chloride was added. The reaction mixture was refluxed for 2 h, cooled to room temperature and filtered. The green filtrate was added to 250 ml concentrated sulphuric acid. The

residue (374 mg) turned out to be unreacted iridiumchloride. The sulphuric-acid solution was diluted to a total volume of 2 l, filtered, washed with water and dried for 7 h at 150°C and 0.1 mbar. Yield 45 mg (<16%, based on reacted amount of iridium chloride). The product is supposed to be IrPc-Cl with a sixth ligand, being a co-ordinating chloride[18] or a dicyanobenzene[17]. The green powder is soluble in acetone. The *uv*-Vis spectrum of concentrated sulphuric acid was in accordance with published data[18].

2.3. Irreversibly adsorbed metal-chelates

These were prepared on freshly polished pyrolytic graphite. The surface was polished with 5 and 0.3 μm alumina, subsequently rinsed with water and sonicated in water for a few minutes. After drying, the electrode was immersed in a solution of the chelate (≈ 1 mg chelate ml solvent^{-1}) for 5 min, rinsed with a small amount of the solvent and dried. CH_2Cl_2 and acetone were used for the porphyrins and phthalocyanine, respectively.

2.4. Carbon-supported catalysts

These (7 wt.% loading) were prepared by forced adsorption of the metal-chelate onto Vulcan XC-72R from ethanol/water[20]. Heat treatment was carried out in a down-flow reactor in an argon atmosphere, deoxygenated using a Cu-tower at 125°C. The flow was 25 ml min^{-1} . The temperature was raised with 10°C min^{-1} up to the desired temperature, kept constant for 2 h, after which the sample was cooled in argon to room temperature. A 5 wt.% iridium/Vulcan catalyst was prepared by incipient wetness impregnation using iridium-chloride, followed by reduction in hydrogen at 500°C.

2.5. Electrochemical measurements

Measurements were performed in a conventional three-electrode cell, using a Tacussel bipotentiostat connected to a Wenking scangenerator. The electrolyte was 0.5 M H_2SO_4 ; a reversible hydrogen elec-

trode was used as reference electrode and a Pt-foil as counter electrode. For rotating ring-disc experiments, the supported catalysts were fitted in the disc electrode by affixing the catalyst to a conducting carbon paste ("leitC") in a disc hole. A platinized ring was used. Prior to each experiment, the ring was reactivated for 15 min by repeated anodic and cathodic pulses of 3 s, 10 mA. During measurement the ring potential was kept constant at 1.3 V vs. *rhe*. The collection factor is 12% for the leitC electrode and 20% for the pyrolytic graphite electrode.

The precise activity was measured with the floating electrode technique[21]. For preparation of the teflon sintered electrodes the catalyst is suspended sonically in water and a diluted teflon (ICI FLUON GP-1) suspension is added (total amount of teflon in the dry sample 20 wt.%). The suspension is filtered through a membrane filter and brought on a small-mesh gold wire-grid (ϕ 10 mm). The electrode was dried and sintered in an argon atmosphere at 325°C for 2 h.

3. RESULTS

3.1. O_2 reduction

The oxygen reduction behaviour of the irreversibly adsorbed Ir-chelates is shown in Fig. 1. At both IrOEP and IrTPP the reduction follows the four-electron pathway, while at IrPc the ring current indicates that hydrogen peroxide is formed. For the Ir-porphyrins an unusual deactivation is observed at lower potentials: during the anodic scan the electrode reactivates to become even more active than in the cathodic scan. At lower scanning rates this difference is smaller. (N.B. during the first cathodic scan no activity at all is found.) The peak maximum shows a linear dependence on the scan rate. The stability of the adsorbed chelates was high.

The behaviour of IrOEP supported on Vulcan does not substantially differ from the adsorbed species on C_p . Heat treatment of IrOEP on Vulcan at different temperatures reveals a (partial) change in mechanism (Fig. 2). The main product of reduction is

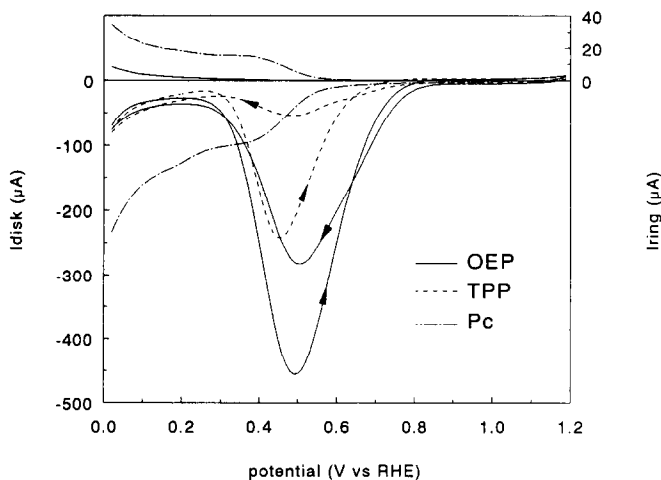


Fig. 1. O_2 reduction at *rde* with irreversibly adsorbed iridium-chelates on C_p : 0.5 M H_2SO_4 , 16 rps, 10 mV s^{-1} .

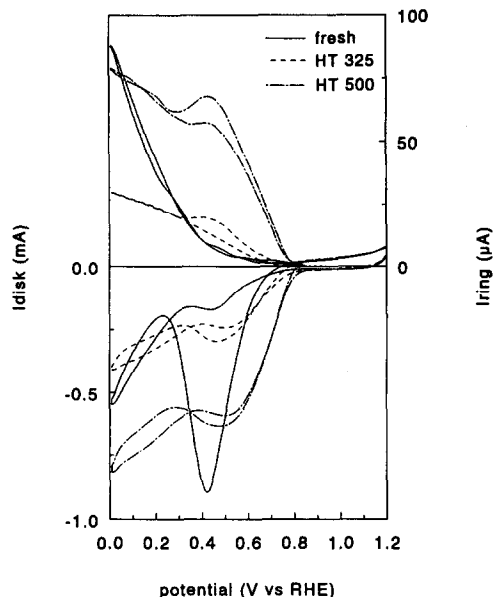


Fig. 2. O_2 reduction at *rde* of heat treated IrOEP/Vulcan: 0.5 M H_2SO_4 , 16 rps, $10 mV s^{-1}$.

now hydrogen peroxide. The temperature at which maximum activity is reached, is relatively low, around 500°C. This pyrolysed catalyst exhibit the highest activity when compared with pyrolysed IrTPP, CoTPP and FeTPP-Cl (Fig. 3). Unfortunately, the Ir-catalysts, including the heat-treated catalysts, are not stable towards prolonged exposure to air, after several months the activity has vanished. In the latter case, the activity can be more or less restored by a second heat treatment. The activity of the carbon supported metallic iridium was found to be far less than that of the heat-treated metal chelates.

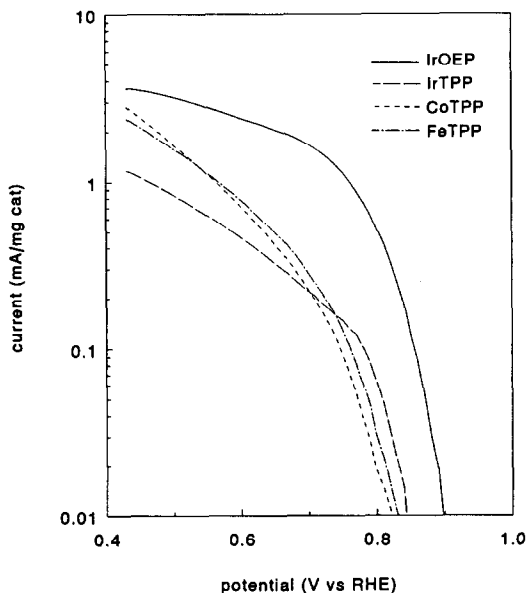


Fig. 3. O_2 reduction at floating electrodes for different heat treated supported chelates: 0.5 M H_2SO_4 , $1 mV s^{-1}$

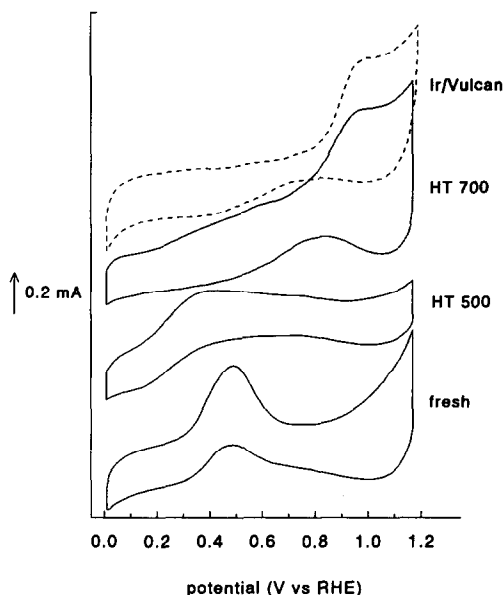


Fig. 4. CO oxidation of heat treated IrOEP/Vulcan: 0.5 M H_2SO_4 , 16 rps, $10 mV s^{-1}$.

3.2. CO oxidation

The oxidation of CO is shown in Fig. 4 for IrOEP/Vulcan. A reversible deactivation at high potentials is observed. Heat treatment results in an increase in activity and a broadening of the active potential range; this behaviour was already observed after pyrolysis at 325°C. Also for IrPc a broad active potential range is observed, albeit with very low activity. At higher temperatures (700°C) the porphyrin apparently decomposes. The CO oxidation feature at high potential observed for such a sample is typical of metallic iridium (verified on our 5 wt.% Ir/Vulcan catalyst, Fig. 4).

4. DISCUSSION

The behaviour of IrOEP and IrTPP in oxygen reduction is similar. This is in contrast with Collman[3] who did not find any oxygen reduction activity for IrTPP. The activity for oxygen reduction is low for all non-pyrolysed iridium-chelates: OEP, TPP and Pc, compared to other metal chelates. No influence of the rotation frequency is observed, the current is totally kinetically limited. In some experiments the iridium-porphyrins could be activated by brief reduction at $-0.2 V$ vs. *rhe*. This might be the same effect as was observed for IrOEP-I by Collman[3]. He ascribed this activation to formation of $(IrOEP)_2$, which is the oxygen accepting molecule in his model. In our view it can be attributed to the disappearance of an axial (chloride) ligand that could not be removed by oxygen. Our assumption is supported by the observation that in 1 M HCl at first no oxygen reduction was observed. After a short cathodic treatment at $-0.2 V$ vs. *rhe*, some activity was measured in the first anodic scan.

An activity maximum is observed in the voltammogram for O_2 reduction and CO oxidation at Ir-porphyrins in the same potential range. A dual site

mechanism has been proposed[3] to explain the four electron reduction of oxygen at IrOEP. However, carbon monoxide can only bind to a single metal site. As the CO oxidation seems to be hampered by the same activation and deactivation processes as the oxygen reduction, this can be considered as an indication that the oxygen reduction may also proceed via a single site mechanism. This also holds for IrTPP which shows the same characteristics. Both the oxygen reduction and carbon monoxide oxidation suffer the same de- and reactivation process. We propose a single site mechanism, consisting of a geometric part to explain the observed selectivity variance and a redox part to explain the observed de- and reactivation.

Oxygen reduction is normally assumed to take place via a redox mechanism[20] in which the central metal ion is involved, here the 2+ and 3+ valency states of Ir are active. In oxygen reduction Ir(II) may be the oxygen accepting site, possibly existing as short-living intermediate since Ir(II) is not a common valency for iridium. In CO oxidation adsorption of CO is known to take place on an Ir(III) site[12, 15]. The remarkable reversible deactivation at lower potentials in oxygen reduction is surmised to be due to such strong oxygen binding on the surface that this site is no longer available for further reaction. A possibility here is the formation of Ir(I)-O₂ on the surface where we then have to assume that the Ir(I)-O₂ species is irreducible. An analogous irreducible species has been surmised for osmium-porphyrins at low potentials[10]. The reversible deactivation at high potentials in CO oxidation is thought to be due to the formation of Ir(IV)=O. The activity observed in the cathodic scan being lower than in the anodic one, and the difference decreasing with decreasing scan rate imply that the reduction of this species is slow. After heat treatment and for IrPc the formation of Ir(IV)=O is suppressed.

In the proposed single site mechanism the iridium is supposed to switch rather easily of valency. However, no redox transitions could be measured in a deoxygenated solution, in contrast with Collman *et al.*[3]. *In situ* Raman spectroscopy on the other hand indicates changes in the oxidation state of the iridium as will be discussed in a forthcoming paper[22]. Moreover, changes in symmetry of the molecule wave not observed, making a monomer-dimer transition unlikely. These results are in favour of a single site mechanism.

The capability to switch easily of valency and the observed selectivity variance may be related to the position of the iridium. An in-plane metal ion is very tightly bound to the chelate and also interacts with the underlying carbon surface, leaving only one co-ordination site to obtain an optimum co-ordination of 6. In contrast, an out-of-plane metal ion is hardly influenced by the support and has two co-ordination sites left. In a porphyrin-ring the iron atom is known to be in out-of-plane position[23]. Since iridium is larger than iron, it is likely to be in an out-of-plane position as well. Due to the two unoccupied co-ordination sites, oxygen can be accepted in a side-on position, facilitating oxygen-oxygen bond cleavage. Side-on adsorption is known to occur for Ir(I)-

diphosphine (Vaska) complexes[24]. In this way, oxygen is reduced to water as a result of the presence of both the out-of-plane iridium and the side-on adsorption of which iridium is capable.

In the phthalocyanine ring, the iridium is supposed to be in an in-plane position[17], here the support acts as axial ligand. So oxygen can only be accepted in a bent position in which oxygen-oxygen bond cleavage is much more difficult and only hydrogen peroxide is formed.

After heat treatment of the carbon supported porphyrins a significantly higher activity is obtained for both CO oxidation and O₂ reduction. At these catalysts the formation of hydrogen peroxide is now observed. This change in mechanism can be explained by a change in position of the iridium. During pyrolysis the chelate undergoes partial disintegration and reacts with the carbon surface. This causes a change in the position of iridium: the ring widens so that the iridium can fit in the ring and bind to the carbon surface. The oxygen reducing site will be a modified IrN₄-moiety and the geometric situation will be similar to that of IrPc.

The mechanism of the oxygen reduction changes remarkably after heat treatment already at low temperature, 325°C. The sintering of the teflon is usually carried out at this temperature and it has been always considered to be low enough not to cause any changes. This assumption now turns out to be incorrect.

If the heat treatment temperature is increased, further distintegration occurs and metallic iridium is formed. As mentioned, metallic iridium is less active in the oxygen reduction reaction. Thus, formation of a metallic phase would not appear to lead to optimum activity, contrary to the opinion expressed by Scherson *et al.*[25] and Martin Alves *et al.*[26].

5. CONCLUSIONS

At IrOEP as well as at IrTPP four-electron reduction of oxygen was observed. However, a peculiar deactivation at low potentials is observed. For the carbon monoxide oxidation a similar active potential range is found, here a deactivation occurs at high potentials. After heat treatment a high oxygen reduction activity is obtained, but the mechanism has changed to two-electron reduction. Unfortunately the catalysts are not stable towards prolonged exposure to air.

The oxygen reduction on iridium sites can be explained with a single site mechanism, taking into account redox transitions to explain the catalytic cycle as well as the de- and reactivation processes and a geometrical description to explain the observed selectivity variance. The position of the iridium is determined if oxygen-oxygen bond cleavage is possible: for the out-of-plane iridium in porphyrins side-on adsorption and water formation occurs, whereas for the in-plane iridium in the phthalocyanine only bent adsorption and hydrogen peroxide formation is found.

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