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Why Cobalt macrocyclic complexes are not efficient catalysts for the oxygen reduction reaction, under acidic conditions.

Claudie Miry[a], Emmanuel Ngameni[b], Frederic Gloaguen[c], Maurice L'Her[c]*.

Laboratoire de chimie, électrochimie moléculaires et chimie analytique - UMR 6521 (UBO - CNRS) Faculté des Sciences et Techniques - 6 Avenue Victor le Gorgeu, 29238 BREST. France. (maurice.lher@univ-brest.fr).

Abstract

The activation of the oxygen reduction reaction (ORR) is of a primary importance for the development of fuel cells. Cobalt macrocyclic complexes, *e.g.* those of porphyrins, phthalocyanines, tetraazaannulenes (TAA), cyclam, have been tested in order to replace platinum, the best catalyst but a rare and expensive metal. However it has been noted in some studies that these complexes suffer from degradation in an acidic environment. Suspicions have already been expressed that such degradation are caused by hydrogen peroxide or demetallation, but the reason for the loss of activity of these catalysts has never been experimentally established. In the present work, it has been clearly demonstrated that cobalt complexes are stable in the presence of acids when the metal centre is at the Co(III) oxidation state but are demetallated when it is reduced to the Co(II) oxidation state, which occurs during the oxygen reduction reaction. Co^{2+} is a borderline Lewis acid in Pearson's classification and thus can be substituted by H^+ in an acidic environment.

Keywords : Oxygen reduction reaction (ORR), cobalt macrocyclic complexes, demetallation, aqueous acidic solution.

Present addresses :

a : Laboratoire d'Analyses, de Surveillance et d'Expertise de la Marine
15bis avenue de l'Ecole Navale - 29 200 BREST – France.

b : Laboratoire de Chimie analytique, Université de Yaoundé 1 – Yaoundé – Cameroun.

1. Introduction

The oxygen reduction reaction (ORR) at electrodes is important for realizing efficient fuel cells. The reduction of dioxygen (O_2) is not easy, due to its electronic configuration and to its high activation energy barrier ; thus, ORR requires to be catalysed [1, 2]. The mediation of a catalyst is required in order to reduce the overpotential of ORR, which causes an important loss of potential in any electrochemical cell including an oxygen electrode, an issue of a primary importance for fuel cells [2]. Platinum is the best catalyst for ORR, a metal rare and of strategic importance and consequently expensive, which is an obstacle to the development of fuel cells. For that reason, the search for efficient substitutes to the precious metal has been intense. The importance of iron porphyrins in the transport and activation of oxygen in biological systems being well known and documented, the possibility to use iron porphyrins as catalysts has been tested, as well as cobalt complexes with porphyrins and other cyclic macrocycles [3-9]. The efficiency of metal complexes for ORR is known since a long time. The role of the metal centre has been scrutinized in many works from which it appears that iron and cobalt complexes are good candidates [10]. The overpotential is reduced when cobalt is the metal centre instead of iron. Accordingly, a huge number of works have been devoted to the study of the efficiency of cobalt(II) complexes. Fuel cells can be operated under various conditions, but for practical reasons, in particular due to the presence of CO_2 in air, the source of oxygen, it is advisable to work under acidic conditions. This of course requires that the complexes must be stable in acid media.

The intent of the present work is not to compare the respective properties of the various metal complexes, or those of their association with the electrodes, in order to orientate the selection of the most appropriate combination for ORR; this has already been extensively documented in an incommensurable number of publications and reviews [11-14]. The purpose of this report is to explain why the cobalt complexes, despite their intrinsic promising qualities for the catalysis of ORR, cannot be efficient catalysts for fuel cells working with acidic electrolytes. Among the huge number of publications devoted to the ORR catalysis by cobalt complexes in acidic conditions, from the 70’s until now, only some of them noted that the intensity of the catalytic current decreased with time along an electrolysis and mentioned the lack of stability of the catalyst. Later on, thermal treatments of the catalysts associated with the electrode material have been proposed in order to make them more stable [14-16]. Neither the improvement of the catalysts nor the result of their evolution under the thermal treatment have however been clearly established [14].

The reason for the loss of efficiency of the cobalt macrocyclic complexes has never been unequivocally demonstrated. Since the early beginning of the studies on N_4 chelates, various hypotheses have been proposed, such as leeching of the catalyst from the electrode, destruction of the organic ligand through its reaction with hydrogen peroxide (H_2O_2) generated at the electrode [14,17]. The loss of metal by protonation of the ligand have been suspected to occur in acidic electrolytes [18]. In the present study, by some experiments with various macrocyclic cobalt complexes, it will be shown that demetallation is the reaction leading to the decrease of the catalytic efficiency and the reason for this will be clarified.

2. Experimental

The cobalt porphyrin CoC_2diE and the cofacial bisporphyrin Co_2FTF_4 are gifts from Pr Collman’s group at Stanford University. CoTAA has been synthetized by refluxing dihydrodibenzo[5,9,14,18]tetraaza[14]annulene and $Co(OCOCH_3)_2$ in DMF under N_2

[19]. Sulfuric and trifluoroacetic acids are commercial products of analytical grade. Ultra-pure water was obtained by reverse osmosis followed by ion exchange (Millipore). N_2 (L'Air Liquide) used for flushing the solutions contains traces of O_2 (≤ 5 ppm).

A potentiostat EG&G-PAR (model 273) has been used for the electrochemical studies. The working electrodes were platinum or vitreous carbon discs. All the potentials in this publication are referred to the normal hydrogen electrode (NHE). The UV-visible spectra were recorded using a Varian spectrophotometer (Cary 219).

3. Results

Co(II) macrocyclic complexes, with ligands such as cofacial bisporphyrins, monoporphyrins, phthalocyanines, cyclams and tetraazaannulenes, have been studied. These works provided valuable information about the behaviour of the cobalt complexes towards the O_2 reduction to water or hydrogen peroxide but demonstrated that the current of electrolysis decreases with time; the loss of efficiency of these complexes must be attributed to their instability in contact with acidic media.

3.1 Tetrazaannulenes (TAA)

Some works have been devoted to Co(II)dibenzotetraaza[14]annulene (TAA) (Scheme 1) and to related compounds.[5, 19, 20, 21] When this catalyst is adsorbed on an edge plane pyrolytic graphite electrode (EPGE) in contact with an aqueous acid solution (0.5 M H_2SO_4, $P(O_2) = 1$ atm), oxygen is reduced to hydrogen peroxide at an onset potential of about 0.7 V [19]. However, upon a second potential scan with the same electrode, the O_2 reduction wave is shifted towards more negative potentials while simultaneously the limiting current decreases. Obviously, the adsorbed catalyst is not really stable and this had already been noted earlier, as well as for other catalysts. Heat treatment improves the stability but still a steady decrease of the catalytic current is observed [14]. M(II)TAA, as well as other substituted TAA complexes, can be electropolymerized, leaving a dense conductive film deposited on the electrode [19, 21]. The formal redox potential for Co(III)/Co(II) is close to 0.65 V for a film of CoTAA. The reduction wave for O_2 is clearly linked to the metal redox system. From 0.75 V to the potential at which is positioned the peak current for the reduction of Co(III), O_2 is reduced to H_2O_2. At more negative potentials, oxygen is reduced to water through the 4-electron mechanism, which is not observed with adsorbed CoTAA. Clearly, this can be attributed to the density of the cobalt sites in the phase deposited by electropolymerization, allowing the cooperation of vicinal metal centres. This has been demonstrated by the copolymerization of CoTAA and other compounds inert for ORR, such as NiTAA and H_2TAA. The more negative wave (4e) decreases with the amount of CoTAA in the film and disappears completely for a mass ratio of CoTAA/H_2TAA = 1/5 (unpublished results). This is an illustration of the importance of the cooperation between two metal centres, the density of the Co centres being too low when CoTAA is copolymerized with a large amount of H_2TAA. We have also previously reported that for CoTAA electropolymerized on roughened GC and on porous electrodes (carbon black powder in a Nafion® film) the number of electrons involved in the ORR catalysis is significantly larger than two, which was ascribed to cooperation between Co centres [21].

Thick poly-CoTAA films can be deposited on a graphite or a glassy carbon electrode by electropolymerization of a saturated CoTAA solution in aqueous 2.25 M H_2SO_4, by cycling between 0 V and 0.95 V [19]. When such a modified electrode is transferred to an aqueous 0.5 M H_2SO_4 solution, cyclic voltammetry shows that both the Co(II) oxidation and the Co(III) reduction peaks are present, superimposed on the important capacitive current; the redox system is chemically reversible (Figure 1). The surface concentrations of CoTAA, in the range of 1×10^{-9} mol cm^{-2} to 7×10^{-9} mol cm^{-2}, have been calculated by integration of the current under the peaks, after deduction of the capacitive current.

Figure 1

The catalytic current of O_2 reduction at a rotating electrode decreases with time, indicating that the catalyst is degraded. In order to investigate the reason for this loss of activity, the poly-CoTAA film was cycled under a nitrogen atmosphere between 0 V and 0.95 V. After 50 cycles, the loss of activity is 15 % and 45 % after 1000 cycles, which demonstrates that the catalyst is degraded by potential cycling even under an inert atmosphere. After immersion of the electrode in an aerated acidic aqueous solution (H_2SO_4 0.5 M) during 24 h, without polarization, the voltammogram recorded under nitrogen is identical to the one of the electrode right after electropolymerization. This latter observation suggests that no demetallation occurs when cobalt is at the Co(III) oxidation state, the most compatible with the presence of O_2. This assumption has been confirmed by cyclic voltammetry (Figure 1). After polarization of the electrode at 0.95 V during 2h30mn (curve b), the peak current is lower than on the voltammogram recorded right after the electropolymerization (curve a). But, after a rest out of the solution the voltammogram recorded under nitrogen proves that all the cobalt sites are still present (curve c). However, after setting the potential of the electrode at 0 V for 2h30mn, in order to bring the metal centres to the Co(II) state, the intensity of the peak is much lower and this loss of activity is irreversible.

The stability of the Co(III) derivatives under acidic conditions has been unambiguously established by the following experiment. A solution of $CoTMTAA(Cl)_2$ in dichloromethane is brought in contact with an aqueous solution of H_2SO_4 (0.5 M) and the complex partitions between the two phases. After a long contact of these solutions with air, during a few hours, the UV-vis spectrum remained unchanged and no $H_2TMTAA(Cl)_2$ appears ; the formation of the protonated macrocycle would have been detected through its intense absorption band at 348 nm.

When an electrode modified by the polymerization of Co(II)TAA is immersed for a long time in an acidic aqueous solution of H_2O_2 (3.10^{-3} M), the voltammogram under nitrogen is identical to the one obtained right after the film formation.

These observations suggest that the catalytic sites are stable when cobalt is at the Co(III) state but readily degrade in the acidic aqueous solution when the metal centre is at the Co(II) state. Moreover, hydrogen peroxide has no deleterious effect.

3.2 Monoporphyrin CoC_2diE

Porphyrins and phthalocyanines have attracted a lot of attention because of their similarity with heme and other molecules involved in some biological processes. It has been shown that cobalt complexes are worth more than the iron ones when the catalysis of the electrochemical reduction of oxygen is the target. Cobalt monoporphyrins, for example CoC_2diE (Scheme 1), catalyze the O_2 electroreduction to hydrogen peroxide in an acidic environment.

Both CoC_2diE and Co_2FTF_4 can be dissolved in highly acidic aqueous solutions, but the concentration of the cofacial derivative remains low, about 10^{-5} M. The experiments described in the present study have been performed in 6 M aqueous solutions of CF_3COOH. The voltammograms in Figure 2 have been obtained at a stationary and at a rotating platinum disk electrode, for a saturated solution of CoC_2diE obtained by dissolution under a constant flow of nitrogen, which takes about 2h.

Figure 2

Two redox systems appear at about 0.6 V and 0.3 V (curve a). The former is almost reversible whereas the latter shows a sharp oxidation peak indicating that the re-oxidation reaction is perturbed by a surface phenomenon. Two redox sites are present in such a molecule, the Co centre and the macrocycle itself. It is known that in the presence of water, Co(II) is oxidized to Co(III) before the oxidation of the porphyrin ring to its radical cation. Moreover, a reduction current is detected below 0.6 V at the rotating electrode (curve b), showing that a mixture of the two redox species of the second redox couple are present. This suggests that in the solution the metal is present as Co(III), as shown by the reduction wave at 0.3 V, the porphyrin being also partially oxidized as $Co(III)C_2diE^{\bullet\,2+}$. The UV-vis spectrum of the solution presents a Soret peak at 405 nm and two well separated bands at 520 nm and 558 nm as well as a weak one at 645 nm, this latter band being typical of the porphyrin radical cation. The presence of two well separated bands in the visible region is an argument for the presence of Co(III) as the two bands are not so well resolved for Co(II) solutions. That spectrum is almost identical with the spectrum of a cobalt(III) octaethylporphyrin obtained by chemical oxidation. The ESR spectrum of the solution obtained by dissolution of CoC_2diE, corresponding to the UV-vis spectrum already described, consists in a unique line at $g = 2.004$ of a 27.96 G line width; this is typical of the radical cation $Co(III)C_2diE^{\bullet\,2+}$ and consistent with the fact that Co(III) is diamagnetic; the presence of Co(II) in the solution would have been revealed by a 8 lines spectrum, due to its 7/2 spin. All these observations support the conclusion that the result of the dissolution of CoC_2diE in 6 M CF_3COOH, under a constant flow of N_2, is a mixture of $Co(III)C_2diE^{+}$ and $Co(III)C_2diE^{\bullet 2+}$. Traces of O_2 in the N_2 flux oxidize the Co(II) porphyrin in this acidic medium along its slow dissolution process. The sharp oxidation peak observed on the voltammogram at 0.3 V results more than probably from the re-oxidation of the insoluble $Co(II)C_2diE$ deposited during the reduction scan.

The UV-vis spectrum recorded after dissolution of $Co(II)C_2diE$ under rigorous exclusion of oxygen, in an N_2 atmosphere box, is totally different. The complete dissolution lasts 12h instead of 2h for the dissolution on the bench, under a constant flow of N_2. The UV-visible spectrum is fully identical to the spectrum of H_2C_2diE, which dissolves instantaneously in 6 M CF_3COOH. These observations suggest that $Co(II)C_2diE$ is demetallated by contact with the acidic aqueous solution, a rather slow reaction, while, when the dissolution is operated on the bench under a constant flow of N_2, the macrocyclic complex is oxidized to $Co(III)C_2diE^{+}$ and $Co(III)C_2diE^{\bullet 2+}$, certainly because of the traces of O_2 present in the gas flow.

3.3 Cofacial bisporphyrins Co_2FTF_4

It has been demonstrated that cofacial bisporphyrins (FTF = face-to-face), *e.g.* Co_2FTF_4 (Scheme 1), drive the reduction to water through the $4e^-$ mechanism, due to the cooperation of the two metal centres, Co(II) being essential for O_2 binding, the second, Co(III) or another Lewis acid, being needed for the rupture of the O–O bond.[22-25]

The dissolution of the cofacial bisporphyrin Co_2FTF_4 in aqueous 6 M CF_3COOH, on the bench under a flow of N_2 takes about 2h. The voltammograms of the solution is presented in Figure 3.

Figure 3

The cyclic voltammogram is typical of the bisporphyrin, identical to the one observed in benzonitrile; the two Co(III)/Co(II) reversible redox systems are visible at about 0.5 V (curve a), the domain of stability of the mixed-valence compound Co(III)Co(II)FTF$_4$ being about 0.34 V. As already observed for Co(II)C$_2$diE, the hydrodynamic voltammogram (curve b) shows that Co(II) has been oxidized to Co(III), the porphyrin moieties being partially oxidized. The dissolution of Co$_2$FTF$_4$ in aqueous 6 M CF$_3$COOH in an N$_2$ atmosphere box is a very slow process. After neutralization by NaHCO$_3$ of the acidic solution thus obtained, the cofacial bisporphyrin is extracted by CH$_2$Cl$_2$. Its UV-vis spectrum (Figure 4) is identical in all respects to the characteristic one of H$_4$FTF$_4$.

Figure 4

It can be concluded that under acidic conditions Co(II)$_2$FTF$_4$, as well as Co(II)C$_2$diE, is oxidized to its Co(III) derivatives in the presence of traces of O$_2$. However, under complete exclusion of O$_2$, these Co(II) porphyrins are demetallated.

4. Discussion

On view of these experimental observations, under acidic conditions, it is evident that the macrocyclic complexes are stable when the metal is Co(III) but are demetallated when it is as present Co(II). The Co^{3+} ion is a much harder Lewis acid than Co^{2+} and for that reason will bind more strongly to the nitrogen hard bases of the macrocycles.

From the works already published and from calculations, it is possible to evaluate the difference of stability between the two complexes of cobalt in their redox state. This can be evaluated from the relative values of E°'(Co^{3+}/Co^{2+}) and E°'(Co^{III}L/Co^{II}L), the formal redox potential of the complex:

$$\mathrm{Log}_{10}[K(\mathrm{Co^{III}L})/K(\mathrm{Co^{II}L})] = [\, E°'(\mathrm{Co^{3+}/Co^{2+}}) - E°'(\mathrm{Co^{III}L/Co^{II}L})]/0.059 \qquad (1)$$

$E°'(Co^{3+}/Co^{2+})$ has been evaluated to be 1.92 V [26], but 1.81 V is a value proposed by some authors [27]. From $E°'(Co^{III}L/Co^{II}L)$ values reported in publications and evaluated in the present work, $Log_{10}[K(Co^{III}L)/K(Co^{II}L)]$ has been calculated and reported in Table 1, assuming that $E°'(Co^{3+}/Co^{2+})] = 1.92$ V.

Table 1

From the experimental data in Table 1 it is clear that, whatever is the nature of the ligand, the Co(III) complexes are much more stable than those of Co(II). In the case of CoTAA, as well as that of CoCyclam, which catalytic properties towards ORR have also been examined [28], DFT calculations confirm the much higher stability of the Co(III) complexes by a factor of 10^{27} and 10^{17}, respectively (Table 1, Supplementary material).

It is not really easy to unambiguously conclude whether the reduction wave of O_2 coincides with the reduction wave of Co(III) to Co(II), as observed with polymerized CoTAA, or occurs at more negative potentials, as reported in some cases [7, 29]. However, in both cases, when ORR occurs the redox state of cobalt in the catalyst is Co(II), which can be easily replaced by two hard acid ions such as H^+. This also should occur in the case of Co(II)Cyclam, which binding constant is K(Co(II)Cyclam) = 10^{14}.[30] The affinity of Cyclam for the proton is high, $K(H_2Cyclam) = 10^{22}$ [31], the consequence being that even a rather concentrated Co(II)Cyclam solution (0.01 M) would be completely demetallated below pH = 4.

These experimental results are in complete opposition to the conclusions previously drawn from DFT calculations about the stability of metalloporphyrins and metallophthalocyanines in acidic media, stating that the metal ions are not replaced by protons at pH = 1 [32].

Reviews on the catalysis of ORR have mentioned that the instability of the non-precious metal catalysts in acidic media could result from the deleterious influence of H_2O_2 or from the replacement of the metal ion by protons [14, 17]. From this work it appears clearly that hydrogen peroxide does not have a major impact on the stability but that Co^{2+} is easily substituted by protons.

5. Conclusion

Co^{3+}, a much harder Lewis acid than Co^{2+}, will bind more strongly to the nitrogen hard bases of the macrocycles and remains bound under acidic conditions. However, H^+ will have a higher affinity than Co^{2+} for the hard base sites of the ligand. It is more than probable that Fe^{2+}, another borderline acid in the classification of Lewis acids, will behave similarly to Co^{2+}, and consequently, what has been observed for the cobalt complexes should also be true for Fe catalysts in an acidic environment. What occurs to the catalysts after an heat-treatment is not really clear but, whether they have been transformed to metallic particles or to any other form, the redox state of the metal compatible with the potential of the oxygen reduction reaction is the M(II) redox state, which explains why these modified catalysts are also prone to demetallation under acidic conditions.

6. Figure captions

Figure 1 Cyclic voltammetry at a graphite electrode covered by a CoTAA film (H_2SO_4 0.5 M, v = 200 mV.s^{-1}, under N_2). a: right after the film formation; b: after a 2h30mn polarization at 0.95 V ; c: after b and 4 days stay in air ; d: after 2h30 min at 0 V.

Figure 2 Voltammetry of CoC_2diE (~10^{-5} M) in an aqueous solution of 6 M CF_3COOH, at a platinum disk electrode. a: cyclic voltammetry (u = 1 µA, v = 100 mV.s^{-1}); b: voltammetry at a rotating electrode (u = 2.5 µA, v = 2 mV.s^{-1}, ω = 400 rpm).

Figure 3 Voltammetry of Co_2FTF_4 (~10^{-5} M) in an aqueous solution of 6 M CF_3COOH, at a platinum disk electrode. a: cyclic voltammetry (u = 0.4 µA, v = 100 mV.s^{-1}); b: voltammetry at a rotating electrode (u = 1 µA, v = 2 mV.s^{-1}, ω = 400 rpm).

Figure 4 UV-vis spectrum of Co_2FTF_4 after extraction with CH_2Cl_2 of a solution obtained by dissolution in an aqueous solution of 6 M CF_3COOH, under a rigorous exclusion of oxygen.

7. Bibliography

[1] M. L'Her, Redox Properties, Electrochemistry of Oxygen, in: A.J. Bard (Ed.) Encyclopedia of Electrochemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2007, pp. bard070005.

[2] M.R. Tarasevich, A. Sadkowski, E. Yeager, Oxygen Electrochemistry, in: B.E. Conway, J.O.M. Bockris, E. Yeager, S.U.M. Khan, R.E. White (Eds.) Comprehensive Treatise of Electrochemistry, Springer US, Boston, MA, 1983, pp. 301-398.

[3] F. Beck, The redox mechanism of the chelate-catalysed oxygen cathode, Journal of Applied Electrochemistry, 7 (1977) 239-245.

[4] A. Bettelheim, R.J.H. Chan, T. Kuwana, Electrocatalysis of oxygen reduction. Part II. Adsorbed cobalt(III) tetrapyridylporphyrin on glassy carbon electrode, Journal of Electroanalytical Chemistry, 99 (1979) 391-397.

[5] I. Bhugun, F.C. Anson, Adsorption on graphite and catalytic reduction of O_2 by the macrocyclic complex of cobalt(II) with 2,3,9,10-tetraphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, Journal of Electroanalytical Chemistry, 430 (1997) 155-161.

[6] J.P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval, F.C. Anson, Electrode Catalysis of the Four-Electron Reduction of Oxygen to Water by Dicobalt Face-to-Face Porphyrins, Journal of the American Chemical Society, 102 (1980) 6027-6036.

[7] R.R. Durand, F.C. Anson, Catalysis of dioxygen reduction at graphite electrodes by an adsorbed cobalt(II) porphyrin, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 134 (1982) 273-289.

[8] R. Jasinski, Cobalt Phthalocyanine as a Fuel Cell Cathode, J. Electrochem. Soc., 112 (1965) 526-528.

[9] P. Gouérec, M. Savy, Oxygen reduction electrocatalysis: ageing of pyrolyzed cobalt macrocycles dispersed on an active carbon, Electrochimica Acta, 44 (1999) 2653-2661.

[10] J.H. Zagal, M.A. Páez, J.F. Silva, Fundamental Aspects on the Catalytic Activity of Metallomacrocyclics for the Electrochemical Reduction of O2, in: J.H. Zagal, F. Bedioui, J.-P. Dodelet (Eds.) N4-Macrocyclic Metal Complexes, Springer New York, New York, NY, 2006, pp. 41-82.

[11] J.H. Zagal, S. Griveau, J.F. Silva, T. Nyokong, F. Bedioui, Metallophthalocyanine-based molecular materials as catalysts for electrochemical reactions, Coordination Chemistry Reviews, 254 (2010) 2755-2791.

[12] Y.M. Zhao, G.Q. Yu, F.F. Wang, P.J. Wei, J.G. Liu, Bioinspired Transition-Metal Complexes as Electrocatalysts for the Oxygen Reduction Reaction, Chem. Eur. J., 25 (2019) 3726-3739.

[13] Z.P. Li, B.H. Liu, The use of macrocyclic compounds as electrocatalysts in fuel cells, Journal of Applied Electrochemistry, 40 (2010) 475-483.

[14] J.-P. Dodelet, Oxygen Reduction in PEM Fuel Cell Conditions: Heat-Treated Non-Precious Metal-N4 Macrocycles and Beyond, in: J.H. Zagal, F. Bedioui, J.-P.

Dodelet (Eds.) N4-Macrocyclic Metal Complexes, Springer New York, New York, NY, 2006, pp. 83-147.

[15] V.S. Bagotsky, M.R. Tarasevitch, K.A. Radyushkina, O.E. Levina, S.I. Andrusyova, Electrocatalysis of the oxygen reduction process on metal chelates in acid electrolyte, Journal of Power Sources, 1977, pp. 233-240.

[16] A. Van der Putten, A. Elzing, W. Visscher, E. Barendrecht, Oxygen reduction on pyrolysed carbon supported metal chelates, Journal of Electroanalytical Chemistry, 1986, pp. 233-244.

[17] F. Jaouen, J.-P. Dodelet, Non-Noble Electrocatalysts for O2 Reduction: How Does Heat Treatment Affect Their Activity and Structure? Part I. Model for Carbon Black Gasification by NH3: Parametric Calibration and Electrochemical Validation, J. Phys. Chem. C, 111 (2007) 5963-5970.

[18] R.R. Durand, J.P. Collman, F.C. Anson, Dissolution of insoluble dicobalt cofacial porphyrins in concentrated acids to produce increased stability in their catalysis of the reduction of dioxygen, Journal of Electroanalytical Chemistry, 151 (1983) 289-294.

[19] C. Miry, D. Le Brun, J.-M. Kerbaol, M. L'Her, Cobalt(II)–dibenzotetraaza[14]annulene complex electropolymerization for electrode modification, Journal of Electroanalytical Chemistry, 494 (2000) 53-59.

[20] I. Bhugun, F.C. Anson, Enhancement of the Catalytic Activity of a Macrocyclic Cobalt(II) Complex for the Electroreduction of O_2 by Adsorption on Graphite, Inorganic Chemistry, 35 (1996) 7253-7259.

[21] P. Convert, C. Coutanceau, P. Crouigneau, F. Gloaguen, C. Lamy, Electrodes modified by electrodeposition of CoTAA complexes as selective oxygen cathodes in a direct methanol fuel cell, J. Appl. Electrochem., 31 (2001) 945-952.

[22] R. Guilard, S. Brandes, C. Tardieux, A. Tabard, M. L'Her, C. Miry, P. Gouerec, Y. Knop, J.P. Collman, Synthesis and Characterization of Cofacial Metallodiporphyrins Involving Cobalt and Lewis Acid Metals: New Dinuclear Multielectron Redox Catalysts of Dioxygen Reduction, J. Am. Chem. Soc., 117 (1995) 11721-11729.

[23] Y. Le Mest, C. Inisan, A. Laouénan, M. L'Her, J. Talarmin, M. El Khalifa, J.-Y. Saillard, Reactivity toward Dioxygen of Dicobalt Face-to-Face Diporphyrins in Aprotic Media. Experimental and Theoretical Aspects. Possible Mechanistic Implication in the Reduction of Dioxygen, J. Am. Chem. Soc., 119 (1997) 6095-6106.

[24] Y. Le Mest, M. L'Her, J.P. Collman, N.H. Hendricks, L. McElwee-White, Remarkable oxygen affinity of a mixed valence dicobalt cofacial porphyrin CoIIICoIIFTF4, J. Am. Chem. Soc., 108 (1986) 533-535.

[25] Y. Le Mest, M. L'Her, J. Courtot-Coupez, J.P. Collman, E.R. Evitt, C.S. Bencosme, Electrochemical behaviour of a binary cofacial dicobalt porphyrin in aprotic media under a nitrogen atmosphere, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 184 (1985) 331-346.

[26] N. Maki, T. Tanaka, Cobalt, in : A. J. Bard, R. Parsons, J. Jordan, IUPAC (Eds) Standard potentials in aqueous solution, M. Dekker, New York, 1985, pp 367-381.

[27] S.G. Bratsch, Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K, Journal of Physical and Chemical Reference Data, 18 (1989) 1-21.

[28] T. Geiger, F.C. Anson, Homogeneous catalysis of the electrochemical reduction of dioxygen by a macrocyclic cobalt(III) complex, J. Am. Chem. Soc., 103 (1981) 7489-7496.

[29] C.L. Ni, F.C. Anson, Relation between the Reduction Potentials of Adsorbed and Unabsorbed Cobalt(III) Ttetrakis(N-methylpyridinium-4-yl)porphyrin and Those Where It Catalyzes the Electroreduction of Dioxygen, Inorganic Chemistry, 24 (1985) 4754-4756.

[30] S. Cabani, N. Ceccanti, G. Conti, Enthalpy Changes in the Binding of O_2 to Co(II) Complexes with 1,4,8,l 1-Tetraazacyclotetradecane, Inorganica Chimica Acta, 1984.

[31] M. Micheloni, A. Sabatini, P. Paoletti, Solution chemistry of macrocycles. Part 1. Basicity constants of 1,4,8,11-tetra-azacyclotetradecane, 1,4,8,12-tetra-azacyclopentadecane, and 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, J. Chem. Soc., Perkin Trans. 2, (1978) 828-830.

[32] Y. Chen, X. Hua, S. Chen, Theoretical study of stability of metal-N4 macrocyclic compounds in acidic media, Chinese Journal of Catalysis, 37 (2016) 1166-1171.

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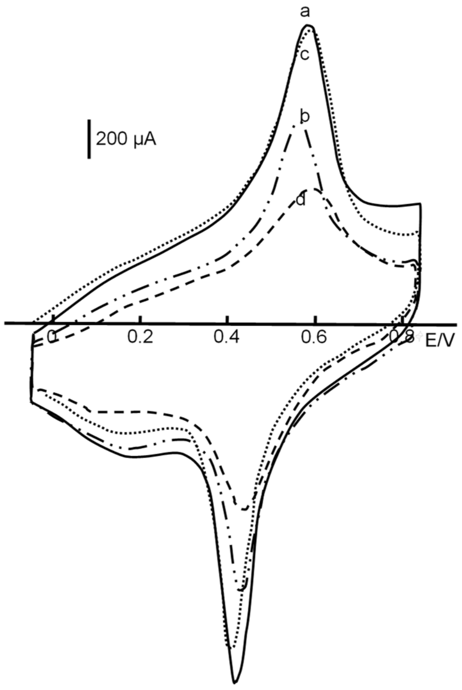

Figure 1 Cyclic voltammetry at a graphite electrode covered by a CoTAA film (H_2SO_4 0.5 M, v = 200 mV.s^{-1}, under N_2). a : right after the film formation ; b : after a 2h30mn polarization at 0.95 V ; c : after b and 4 days stay in air ; d : after 2h30 mn at 0 V.

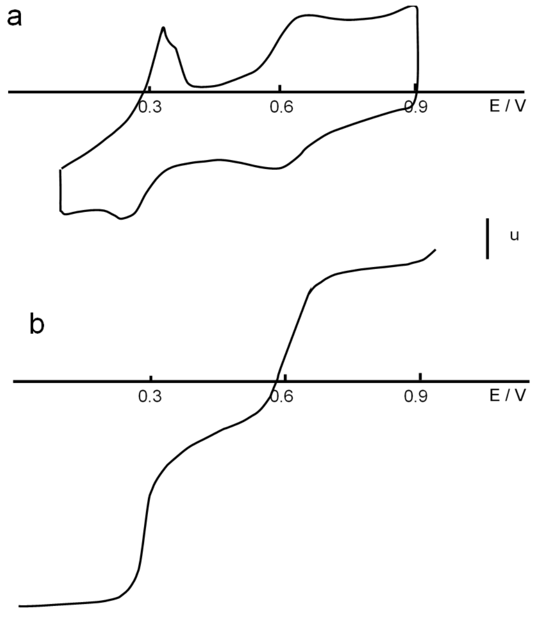

Figure 2 Voltammetry of CoC_2diE (~10^{-5} M) in an aqueous solution of 6 M CF_3COOH, at a platinum disk electrode. a : cyclic voltammetry (u = 1 µA, v = 100 mV.s^{-1}); b : voltammetry at a rotating electrode (u = 2.5 µA, v = 2 mV.s^{-1}, ω = 400 rpm).

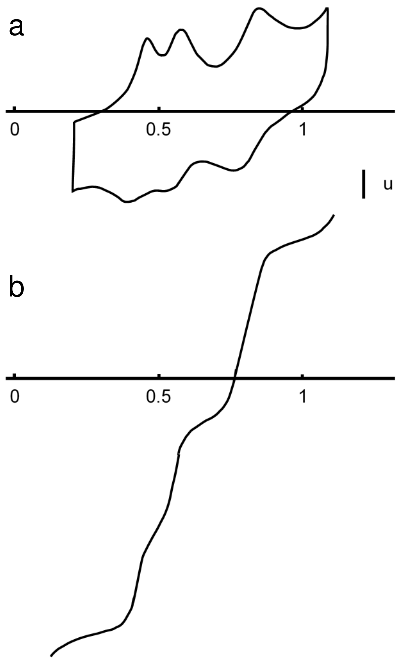

Figure 3 Voltammetry of Co_2FTF_4 (~10^{-5} M) in an aqueous solution of 6 M CF_3COOH, at a platinum disk electrode. a : cyclic voltammetry (u = 0.4 µA, v = 100 mV.s^{-1}); b : voltammetry at a rotating electrode (u = 1 µA, v = 2 mV.s^{-1}, ω = 400 rpm).

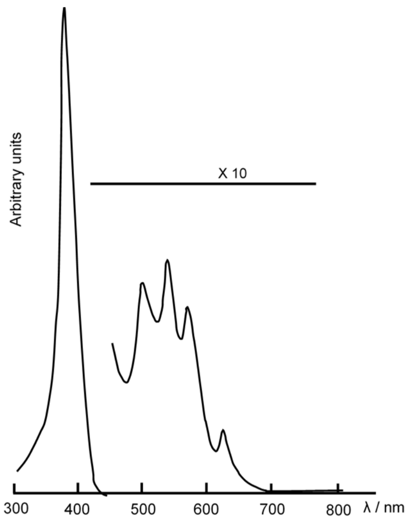

Figure 4 UV-vis spectrum of Co_2FTF_4 after extraction with CH_2Cl_2 of a solution obtained by dissolution in an aqueous solution of 6 M CF_3COOH, under a rigorous exclusion of oxygen.

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Table 1: Relative stabilities of some Co(III) and Co(II) complexes.

Ligand[a]	$E°'(Co^{3+}L/Co^{2+}L)$ /V	$Log_{10}[K(Co^{3+}L)/K(Co^{2+}L)]$ (exp.)[b]	$Log_{10}[K(Co^{3+}L)/K(Co^{2+}L)]$ (DFT)[c]	Ref.
ox_3	0.57	22.9		[26]
$edta_2$	0.38	26.1		[26]
$terpy_2$	0.31	27.3		[26]
cyclam	0.40	25.8	17.1	[26]
TAA	0.58 a	22.7	27.1	this work
C_2diE	0.29 a	27.7		this work
FTF_4	0.55 a	23.2		this work

[a] Ox, oxalate ion ; edta, ethylenediaminetetraacetate ion ; terpy, 2,2',2''-terpyridine ; cyclam, 1,4,8,11-tetraazacyclotetradecane ; TAA, $(benzo)_2[14]tetraeneN_4$; C_2diE, diethylester mesoporphyrin ; FTF_4, face-to-face bisporphyrin. [b] Calculated from the experimental values of $E°'(Co^{3+}L/Co^{2+}L)$ due to the rather poor solubility of the compound in the aqueous acid solution, the uncertainty on these redox potential is not less than ± 0.02 V. [c] Calculated from the DFT values of $E^0(Co^{3+}/Co^{2+})$.