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Claudie Miry, Emmanuel Ngameni, Frédéric Gloaguen, Maurice L'her. Why Cobalt macrocyclic complexes are not efficient catalysts for the oxygen reduction reaction, under acidic conditions. *Electrochimica Acta*, 2020, 358, pp.136854. 10.1016/j.electacta.2020.136854 . hal-02939303

**HAL Id: hal-02939303**

**<https://hal.univ-brest.fr/hal-02939303>**

Submitted on 26 Aug 2022

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

3

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8

9 **Abstract**

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

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

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## 1        **1. Introduction**

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

23       The intent of the present work is not to compare the respective properties of the  
24       various metal complexes, or those of their association with the electrodes, in order to  
25       orientate the selection of the most appropriate combination for ORR; this has already

1 been extensively documented in an incommensurable number of publications and  
2 reviews [11-14]. The purpose of this report is to explain why the cobalt complexes,  
3 despite their intrinsic promising qualities for the catalysis of ORR, cannot be efficient  
4 catalysts for fuel cells working with acidic electrolytes. Among the huge number of  
5 publications devoted to the ORR catalysis by cobalt complexes in acidic conditions,  
6 from the 70's until now, only some of them noted that the intensity of the catalytic  
7 current decreased with time along an electrolysis and mentioned the lack of stability  
8 of the catalyst. Later on, thermal treatments of the catalysts associated with the  
9 electrode material have been proposed in order to make them more stable [14-16].  
10 Neither the improvement of the catalysts nor the result of their evolution under the  
11 thermal treatment have however been clearly established [14].

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

## 21 **2. Experimental**

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

1 [19]. Sulfuric and trifluoroacetic acids are commercial products of analytical grade.  
2 Ultra-pure water was obtained by reverse osmosis followed by ion exchange  
3 (Millipore). N<sub>2</sub> (L'Air Liquide) used for flushing the solutions contains traces of O<sub>2</sub> ( $\leq 5$   
4 ppm).

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

9

### 10 **3. Results**

11 Co(II) macrocyclic complexes, with ligands such as cofacial bisporphyrins,  
12 monoporphyrins, phthalocyanines, cyclams and tetraazaannulenes, have been  
13 studied. These works provided valuable information about the behaviour of the cobalt  
14 complexes towards the O<sub>2</sub> reduction to water or hydrogen peroxide but demonstrated  
15 that the current of electrolysis decreases with time; the loss of efficiency of these  
16 complexes must be attributed to their instability in contact with acidic media.

#### 17 **3.1 Tetraazaannulenes (TAA)**

18 Some works have been devoted to Co(II)dibenzotetraaza[14]annulene (TAA)  
19 (Scheme 1) and to related compounds.[5, 19, 20, 21] When this catalyst is adsorbed  
20 on an edge plane pyrolytic graphite electrode (EPGE) in contact with an aqueous  
21 acid solution (0.5 M H<sub>2</sub>SO<sub>4</sub>, P(O<sub>2</sub>) = 1 atm), oxygen is reduced to hydrogen peroxide  
22 at an onset potential of about 0.7 V [19]. However, upon a second potential scan with  
23 the same electrode, the O<sub>2</sub> reduction wave is shifted towards more negative  
24 potentials while simultaneously the limiting current decreases. Obviously, the

1 adsorbed catalyst is not really stable and this had already been noted earlier, as well  
2 as for other catalysts. Heat treatment improves the stability but still a steady  
3 decrease of the catalytic current is observed [14]. M(II)TAA, as well as other  
4 substituted TAA complexes, can be electropolymerized, leaving a dense conductive  
5 film deposited on the electrode [19, 21]. The formal redox potential for Co(III)/Co(II) is  
6 close to 0.65 V for a film of CoTAA. The reduction wave for O<sub>2</sub> is clearly linked to the  
7 metal redox system. From 0.75 V to the potential at which is positioned the peak  
8 current for the reduction of Co(III), O<sub>2</sub> is reduced to H<sub>2</sub>O<sub>2</sub>. At more negative  
9 potentials, oxygen is reduced to water through the 4-electron mechanism, which is  
10 not observed with adsorbed CoTAA. Clearly, this can be attributed to the density of  
11 the cobalt sites in the phase deposited by electropolymerization, allowing the  
12 cooperation of vicinal metal centres. This has been demonstrated by the  
13 copolymerization of CoTAA and other compounds inert for ORR, such as NiTAA and  
14 H<sub>2</sub>TAA. The more negative wave (4e) decreases with the amount of CoTAA in the  
15 film and disappears completely for a mass ratio of CoTAA/H<sub>2</sub>TAA = 1/5 (unpublished  
16 results). This is an illustration of the importance of the cooperation between two  
17 metal centres, the density of the Co centres being too low when CoTAA is  
18 copolymerized with a large amount of H<sub>2</sub>TAA. We have also previously reported that  
19 for CoTAA electropolymerized on roughened GC and on porous electrodes (carbon  
20 black powder in a Nafion® film) the number of electrons involved in the ORR  
21 catalysis is significantly larger than two, which was ascribed to cooperation between  
22 Co centres [21].

23 Thick poly-CoTAA films can be deposited on a graphite or a glassy carbon electrode  
24 by electropolymerization of a saturated CoTAA solution in aqueous 2.25 M H<sub>2</sub>SO<sub>4</sub>, by  
25 cycling between 0 V and 0.95 V [19]. When such a modified electrode is transferred

1 to an aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, cyclic voltammetry shows that both the Co(II)  
2 oxidation and the Co(III) reduction peaks are present, superimposed on the important  
3 capacitive current; the redox system is chemically reversible (Figure 1). The surface  
4 concentrations of CoTAA, in the range of  $1 \times 10^{-9}$  mol cm<sup>-2</sup> to  $7 \times 10^{-9}$  mol cm<sup>-2</sup>, have  
5 been calculated by integration of the current under the peaks, after deduction of the  
6 capacitive current.

### 7 Figure 1

8 The catalytic current of O<sub>2</sub> reduction at a rotating electrode decreases with time,  
9 indicating that the catalyst is degraded. In order to investigate the reason for this loss  
10 of activity, the poly-CoTAA film was cycled under a nitrogen atmosphere between 0 V  
11 and 0.95 V. After 50 cycles, the loss of activity is 15 % and 45 % after 1000 cycles,  
12 which demonstrates that the catalyst is degraded by potential cycling even under an  
13 inert atmosphere. After immersion of the electrode in an aerated acidic aqueous  
14 solution (H<sub>2</sub>SO<sub>4</sub> 0.5 M) during 24 h, without polarization, the voltammogram recorded  
15 under nitrogen is identical to the one of the electrode right after  
16 electropolymerization. This latter observation suggests that no demetallation occurs  
17 when cobalt is at the Co(III) oxidation state, the most compatible with the presence of  
18 O<sub>2</sub>. This assumption has been confirmed by cyclic voltammetry (Figure 1). After  
19 polarization of the electrode at 0.95 V during 2h30mn (curve b), the peak current is  
20 lower than on the voltammogram recorded right after the electropolymerization (curve  
21 a). But, after a rest out of the solution the voltammogram recorded under nitrogen  
22 proves that all the cobalt sites are still present (curve c). However, after setting the  
23 potential of the electrode at 0 V for 2h30mn, in order to bring the metal centres to the  
24 Co(II) state, the intensity of the peak is much lower and this loss of activity is  
25 irreversible.



1 The stability of the Co(III) derivatives under acidic conditions has been  
2 unambiguously established by the following experiment. A solution of  $\text{CoTMTAA}(\text{Cl})_2$   
3 in dichloromethane is brought in contact with an aqueous solution of  $\text{H}_2\text{SO}_4$  (0.5 M)  
4 and the complex partitions between the two phases. After a long contact of these  
5 solutions with air, during a few hours, the UV-vis spectrum remained unchanged and  
6 no  $\text{H}_2\text{TMTAA}(\text{Cl})_2$  appears ; the formation of the protonated macrocycle would have  
7 been detected through its intense absorption band at 348 nm.

8 When an electrode modified by the polymerization of  $\text{Co}(\text{II})\text{TAA}$  is immersed for a  
9 long time in an acidic aqueous solution of  $\text{H}_2\text{O}_2$  ( $3 \cdot 10^{-3}$  M), the voltammogram under  
10 nitrogen is identical to the one obtained right after the film formation.

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

### 14 3.2 Monoporphyrin $\text{CoC}_2\text{diE}$

15 Porphyrins and phthalocyanines have attracted a lot of attention because of their  
16 similarity with heme and other molecules involved in some biological processes. It  
17 has been shown that cobalt complexes are worth more than the iron ones when the  
18 catalysis of the electrochemical reduction of oxygen is the target. Cobalt  
19 monoporphyrins, for example  $\text{CoC}_2\text{diE}$  (Scheme 1), catalyze the  $\text{O}_2$  electroreduction  
20 to hydrogen peroxide in an acidic environment.

21 Both  $\text{CoC}_2\text{diE}$  and  $\text{Co}_2\text{FTF}_4$  can be dissolved in highly acidic aqueous solutions, but  
22 the concentration of the cofacial derivative remains low, about  $10^{-5}$  M. The  
23 experiments described in the present study have been performed in 6 M aqueous  
24 solutions of  $\text{CF}_3\text{COOH}$ . The voltammograms in Figure 2 have been obtained at a

1 stationary and at a rotating platinum disk electrode, for a saturated solution of  
2  $\text{CoC}_2\text{diE}$  obtained by dissolution under a constant flow of nitrogen, which takes about  
3 2h.

#### 4 Figure 2

5 Two redox systems appear at about 0.6 V and 0.3 V (curve a). The former is almost  
6 reversible whereas the latter shows a sharp oxidation peak indicating that the re-  
7 oxidation reaction is perturbed by a surface phenomenon. Two redox sites are  
8 present in such a molecule, the Co centre and the macrocycle itself. It is known that  
9 in the presence of water, Co(II) is oxidized to Co(III) before the oxidation of the  
10 porphyrin ring to its radical cation. Moreover, a reduction current is detected below  
11 0.6 V at the rotating electrode (curve b), showing that a mixture of the two redox  
12 species of the second redox couple are present. This suggests that in the solution  
13 the metal is present as Co(III), as shown by the reduction wave at 0.3 V, the  
14 porphyrin being also partially oxidized as  $\text{Co(III)C}_2\text{diE}^{\bullet 2+}$ . The UV-vis spectrum of the  
15 solution presents a Soret peak at 405 nm and two well separated bands at 520 nm  
16 and 558 nm as well as a weak one at 645 nm, this latter band being typical of the  
17 porphyrin radical cation. The presence of two well separated bands in the visible  
18 region is an argument for the presence of Co(III) as the two bands are not so well  
19 resolved for Co(II) solutions. That spectrum is almost identical with the spectrum of a  
20 cobalt(III) octaethylporphyrin obtained by chemical oxidation. The ESR spectrum of  
21 the solution obtained by dissolution of  $\text{CoC}_2\text{diE}$ , corresponding to the UV-vis  
22 spectrum already described, consists in a unique line at  $g = 2.004$  of a 27.96 G line  
23 width; this is typical of the radical cation  $\text{Co(III)C}_2\text{diE}^{\bullet 2+}$  and consistent with the fact  
24 that Co(III) is diamagnetic; the presence of Co(II) in the solution would have been  
25 revealed by a 8 lines spectrum, due to its  $7/2$  spin. All these observations support the

1 conclusion that the result of the dissolution of  $\text{CoC}_2\text{diE}$  in 6 M  $\text{CF}_3\text{COOH}$ , under a  
2 constant flow of  $\text{N}_2$ , is a mixture of  $\text{Co(III)C}_2\text{diE}^+$  and  $\text{Co(III)C}_2\text{diE}^{\cdot 2+}$ . Traces of  $\text{O}_2$  in  
3 the  $\text{N}_2$  flux oxidize the  $\text{Co(II)}$  porphyrin in this acidic medium along its slow dissolution  
4 process. The sharp oxidation peak observed on the voltammogram at 0.3 V results  
5 more than probably from the re-oxidation of the insoluble  $\text{Co(II)C}_2\text{diE}$  deposited  
6 during the reduction scan.

7 The UV-vis spectrum recorded after dissolution of  $\text{Co(II)C}_2\text{diE}$  under rigorous  
8 exclusion of oxygen, in an  $\text{N}_2$  atmosphere box, is totally different. The complete  
9 dissolution lasts 12h instead of 2h for the dissolution on the bench, under a constant  
10 flow of  $\text{N}_2$ . The UV-visible spectrum is fully identical to the spectrum of  $\text{H}_2\text{C}_2\text{diE}$ ,  
11 which dissolves instantaneously in 6 M  $\text{CF}_3\text{COOH}$ . These observations suggest that  
12  $\text{Co(II)C}_2\text{diE}$  is demetallated by contact with the acidic aqueous solution, a rather slow  
13 reaction, while, when the dissolution is operated on the bench under a constant flow  
14 of  $\text{N}_2$ , the macrocyclic complex is oxidized to  $\text{Co(III)C}_2\text{diE}^+$  and  $\text{Co(III)C}_2\text{diE}^{\cdot 2+}$ ,  
15 certainly because of the traces of  $\text{O}_2$  present in the gas flow.

### 16 3.3 Cofacial bisporphyrins $\text{Co}_2\text{FTF}_4$

17 It has been demonstrated that cofacial bisporphyrins (FTF = face-to-face), *e.g.*  
18  $\text{Co}_2\text{FTF}_4$  (Scheme 1), drive the reduction to water through the  $4e^-$  mechanism, due to  
19 the cooperation of the two metal centres,  $\text{Co(II)}$  being essential for  $\text{O}_2$  binding, the  
20 second,  $\text{Co(III)}$  or another Lewis acid, being needed for the rupture of the O–O  
21 bond.[22-25]

22 The dissolution of the cofacial bisporphyrin  $\text{Co}_2\text{FTF}_4$  in aqueous 6 M  $\text{CF}_3\text{COOH}$ , on  
23 the bench under a flow of  $\text{N}_2$  takes about 2h. The voltammograms of the solution is  
24 presented in Figure 3.

## Figure 3

1  
2 The cyclic voltammogram is typical of the bisporphyrin, identical to the one observed  
3 in benzonitrile; the two Co(III)/Co(II) reversible redox systems are visible at about 0.5  
4 V (curve a), the domain of stability of the mixed-valence compound Co(III)Co(II)FTF<sub>4</sub>  
5 being about 0.34 V. As already observed for Co(II)C<sub>2</sub>diE, the hydrodynamic  
6 voltammogram (curve b) shows that Co(II) has been oxidized to Co(III), the porphyrin  
7 moieties being partially oxidized. The dissolution of Co<sub>2</sub>FTF<sub>4</sub> in aqueous 6 M  
8 CF<sub>3</sub>COOH in an N<sub>2</sub> atmosphere box is a very slow process. After neutralization by  
9 NaHCO<sub>3</sub> of the acidic solution thus obtained, the cofacial bisporphyrin is extracted by  
10 CH<sub>2</sub>Cl<sub>2</sub>. Its UV-vis spectrum (Figure 4) is identical in all respects to the characteristic  
11 one of H<sub>4</sub>FTF<sub>4</sub>.

## Figure 4

12  
13 It can be concluded that under acidic conditions Co(II)<sub>2</sub>FTF<sub>4</sub>, as well as Co(II)C<sub>2</sub>diE,  
14 is oxidized to its Co(III) derivatives in the presence of traces of O<sub>2</sub>. However, under  
15 complete exclusion of O<sub>2</sub>, these Co(II) porphyrins are demetallated.

#### 16 4. Discussion

17 On view of these experimental observations, under acidic conditions, it is evident that  
18 the macrocyclic complexes are stable when the metal is Co(III) but are demetallated  
19 when it is as present Co(II). The Co<sup>3+</sup> ion is a much harder Lewis acid than Co<sup>2+</sup> and  
20 for that reason will bind more strongly to the nitrogen hard bases of the macrocycles.  
21 From the works already published and from calculations, it is possible to evaluate the  
22 difference of stability between the two complexes of cobalt in their redox state. This  
23 can be evaluated from the relative values of E°(Co<sup>3+</sup>/Co<sup>2+</sup>) and E°(Co<sup>III</sup>L/Co<sup>II</sup>L), the  
24 formal redox potential of the complex:

$$\text{Log}_{10}[\text{K}(\text{Co}^{\text{III}}\text{L})/\text{K}(\text{Co}^{\text{II}}\text{L})] = [E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+}) - E^{\circ}(\text{Co}^{\text{III}}\text{L}/\text{Co}^{\text{II}}\text{L})]/0.059 \quad (1)$$

$E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+})$  has been evaluated to be 1.92 V [26], but 1.81 V is a value proposed by some authors [27]. From  $E^{\circ}(\text{Co}^{\text{III}}\text{L}/\text{Co}^{\text{II}}\text{L})$  values reported in publications and evaluated in the present work,  $\text{Log}_{10}[\text{K}(\text{Co}^{\text{III}}\text{L})/\text{K}(\text{Co}^{\text{II}}\text{L})]$  has been calculated and reported in Table 1, assuming that  $E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+}) = 1.92$  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  $\text{O}_2$  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  $\text{H}^+$ . This also should occur in the case of Co(II)Cyclam, which binding constant is  $\text{K}(\text{Co}(\text{II})\text{Cyclam}) = 10^{14}$ . [30] The affinity of Cyclam for the proton is high,  $\text{K}(\text{H}_2\text{Cyclam}) = 10^{22}$  [31], the consequence being that even a rather concentrated Co(II)Cyclam solution (0.01 M) would be completely demetallated below  $\text{pH} = 4$ .

These experimental results are in complete opposition to the conclusions previously drawn from DFT calculations about the stability of metalloporphyrins and

1 metallophthalocyanines in acidic media, stating that the metal ions are not replaced  
2 by protons at pH = 1 [32].

3 Reviews on the catalysis of ORR have mentioned that the instability of the non-  
4 precious metal catalysts in acidic media could result from the deleterious influence of  
5 H<sub>2</sub>O<sub>2</sub> or from the replacement of the metal ion by protons [14, 17]. From this work it  
6 appears clearly that hydrogen peroxide does not have a major impact on the stability  
7 but that Co<sup>2+</sup> is easily substituted by protons.

## 8 **5. Conclusion**

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

20

## 1        6. Figure captions

2        Figure 1        Cyclic voltammetry at a graphite electrode covered by a CoTAA film  
3        ( $\text{H}_2\text{SO}_4$  0.5 M,  $v = 200 \text{ mV}\cdot\text{s}^{-1}$ , under  $\text{N}_2$ ). a: right after the film formation; b: after a  
4        2h30mn polarization at 0.95 V ; c: after b and 4 days stay in air ; d: after 2h30 min at  
5        0 V.

6

7        Figure 2        Voltammetry of  $\text{CoC}_2\text{diE}$  ( $\sim 10^{-5} \text{ M}$ ) in an aqueous solution of 6 M  
8         $\text{CF}_3\text{COOH}$ , at a platinum disk electrode. a: cyclic voltammetry ( $u = 1 \mu\text{A}$ ,  $v = 100$   
9         $\text{mV}\cdot\text{s}^{-1}$ ); b: voltammetry at a rotating electrode ( $u = 2.5 \mu\text{A}$ ,  $v = 2 \text{ mV}\cdot\text{s}^{-1}$ ,  $\omega = 400$   
10       rpm).

11

12       Figure 3        Voltammetry of  $\text{Co}_2\text{FTF}_4$  ( $\sim 10^{-5} \text{ M}$ ) in an aqueous solution of 6 M  
13        $\text{CF}_3\text{COOH}$ , at a platinum disk electrode. a: cyclic voltammetry ( $u = 0.4 \mu\text{A}$ ,  $v = 100$   
14        $\text{mV}\cdot\text{s}^{-1}$ ); b: voltammetry at a rotating electrode ( $u = 1 \mu\text{A}$ ,  $v = 2 \text{ mV}\cdot\text{s}^{-1}$ ,  $\omega = 400 \text{ rpm}$ ).

15

16       Figure 4        UV-vis spectrum of  $\text{Co}_2\text{FTF}_4$  after extraction with  $\text{CH}_2\text{Cl}_2$  of a solution  
17       obtained by dissolution in an aqueous solution of 6 M  $\text{CF}_3\text{COOH}$ , under a rigorous  
18       exclusion of oxygen.

19

20

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Ms. Ref. No.: EA20-02870

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

Electrochimica Acta

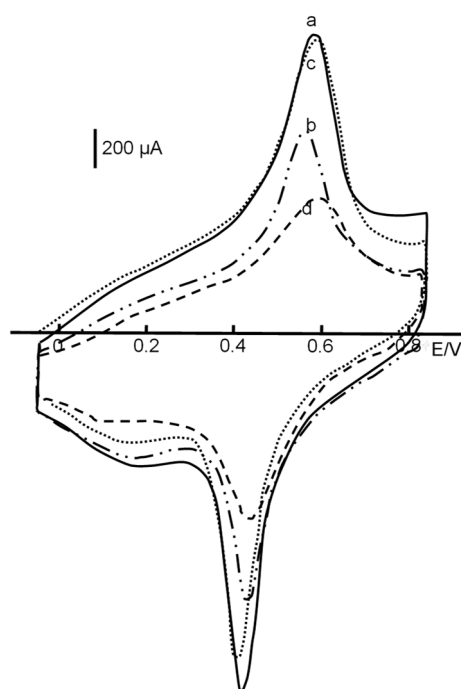


Figure 1 Cyclic voltammetry at a graphite electrode covered by a CoTAA film ( $\text{H}_2\text{SO}_4$  0.5 M,  $v = 200 \text{ mV}\cdot\text{s}^{-1}$ , under  $\text{N}_2$ ). a : right after the film formation ; b : after a 2h30mn polarization at 0.95 V ; c : after b and 4 days stay in air ; d : after 2h30 mn at 0 V.

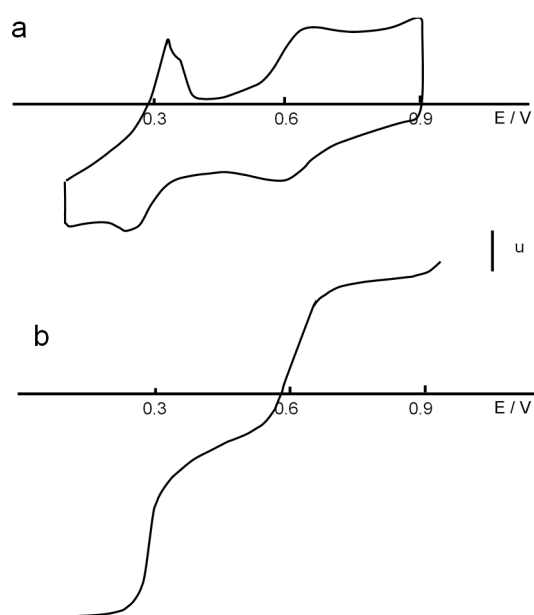


Figure 2 Voltammetry of  $\text{CoC}_2\text{diE}$  ( $\sim 10^{-5}$  M) in an aqueous solution of 6 M  $\text{CF}_3\text{COOH}$ , at a platinum disk electrode. a : cyclic voltammetry ( $u = 1 \mu\text{A}$ ,  $v = 100 \text{ mV}\cdot\text{s}^{-1}$ ); b : voltammetry at a rotating electrode ( $u = 2.5 \mu\text{A}$ ,  $v = 2 \text{ mV}\cdot\text{s}^{-1}$ ,  $\omega = 400 \text{ rpm}$ ).

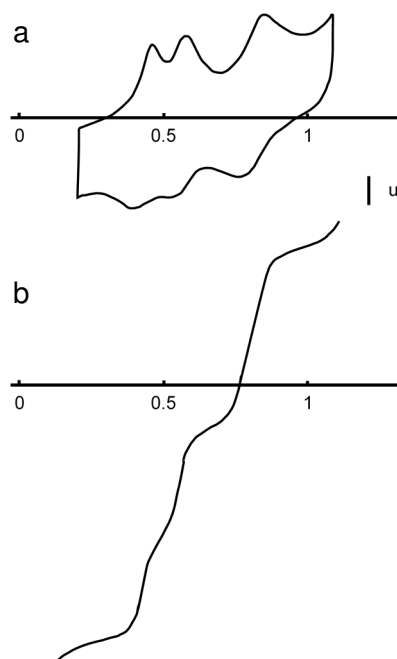


Figure 3 Voltammetry of  $\text{Co}_2\text{FTF}_4$  ( $\sim 10^{-5}$  M) in an aqueous solution of 6 M  $\text{CF}_3\text{COOH}$ , at a platinum disk electrode. a : cyclic voltammetry ( $u = 0.4 \mu\text{A}$ ,  $v = 100 \text{ mV}\cdot\text{s}^{-1}$ ); b : voltammetry at a rotating electrode ( $u = 1 \mu\text{A}$ ,  $v = 2 \text{ mV}\cdot\text{s}^{-1}$ ,  $\omega = 400 \text{ rpm}$ ).

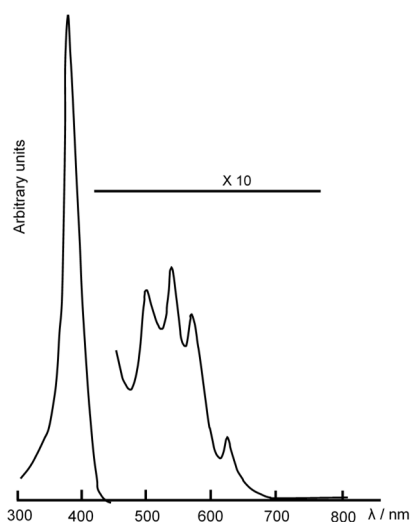


Figure 4 UV-vis spectrum of  $\text{Co}_2\text{FTF}_4$  after extraction with  $\text{CH}_2\text{Cl}_2$  of a solution obtained by dissolution in an aqueous solution of 6 M  $\text{CF}_3\text{COOH}$ , under a rigorous exclusion of oxygen.

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

Ligand <sup>a</sup>	$E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+}) / \text{V}$	$\text{Log}_{10}[\text{K}(\text{Co}^{3+})/\text{K}(\text{Co}^{2+})]$		Ref.
		(exp.) <sup>b</sup>	(DFT) <sup>c</sup>	
ox <sub>3</sub>	0.57	22.9		[26]
edta <sub>2</sub>	0.38	26.1		[26]
terpy <sub>2</sub>	0.31	27.3		[26]
cyclam	0.40	25.8	17.1	[26]
TAA	0.58 a	22.7	27.1	this work
C <sub>2</sub> diE	0.29 a	27.7		this work
FTF <sub>4</sub>	0.55 a	23.2		this work

<sup>a</sup> Ox, oxalate ion ; edta, ethylenediaminetetraacetate ion ; terpy, 2,2',2''-terpyridine ; cyclam, 1,4,8,11-tetraazacyclotetradecane ; TAA, (benzo)<sub>2</sub>[14]tetraeneN<sub>4</sub> ; C<sub>2</sub>diE, diethylester mesoporphyrin ; FTF<sub>4</sub>, face-to-face bisporphyrin. <sup>b</sup> Calculated from the experimental values of  $E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+})$  due to the rather poor solubility of the compound in the aqueous acid solution, the uncertainty on these redox potential is not less than  $\pm 0.02$  V. <sup>c</sup> Calculated from the DFT values of  $E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+})$ .