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Effect of film thickness on the electro-reduction of molecular oxygen on electropolymerized cobalt tetra-aminophthalocyanine films

Abstract We studied the electrocatalytic activity of cobalt tetra-aminophthalocyanine (CoTAPc) for the reduction of molecular oxygen (O_2) on adsorbed monomeric and on electropolymerized films of different thicknesses on glassy carbon (GC) electrode. The polymeric films, denoted poly-CoTAPc, were first characterized by electrochemical impedance spectroscopy and it appears that the types of phenomena revealed to be occurring depend less on the film thickness in basic than in acid media. For O_2 reduction, the results showed that poly-CoTAPc is more active than the monomeric Co-TAPc adsorbed on GC. Indeed, rotating ring-disk electrode data showed that polymeric CoTAPc promotes the four-electron reduction of O_2 to water in parallel to a two-electron reduction to give peroxide. On monomeric and thin films of poly-CoTAPc, a two-electron reduction mechanism predominates. In basic media the activity increases very slightly with thickness, whereas in acid media this increase is more pronounced. This parallels the observed behavior revealed by electrochemical impedance spectroscopy.

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Introduction

For many years, metallophthalocyanines have attracted and continue to attract the attention of authors in electrochemistry for their catalytic properties for the promotion of several electrochemical reactions [1, 2]. In particular, there have been many applications in the use of these complexes as active materials for the reduction of O_2 and their potential applications in fuel cells [3, 4, 5, 6, 7]. In the particular case of cobalt phthalocyanines and substituted derivatives, it is known that they catalyze the reduction of molecular oxygen only to peroxide, via the transfer of two electrons [1, 2] without involving the rupture of the O-O bond. This is not a desirable situation in a fuel cell, since less energy is released at the O_2 cathode [2, 3, 4, 5, 6, 7]. However, with cobalt phthalocyanines there are a very few examples where a four-electron reduction to water has been reported [8, 9, 10, 11, 12, 13]. In these cases, cobalt complexes trapped in conductive polymeric matrices [11], monomeric bilayers of cobalt naphthalocyanines [12] or polymerized materials obtained from the electrochemical oxidation of cobalt tetra-aminophthalocyanine (CoTAPc) [13] were involved. The reasons for obtaining four-electron reduction pathways for O_2 reduction on the latter cobalt phthalocyanine systems remain unclear [8, 9, 10, 11, 12, 13]. However, four-electron reduction pathways for O_2 reduction on dimeric face to face cobalt porphyrins was reported by Anson et al. [14, 15, 16], where the Co-Co separation was tailored to fit and bind the dioxygen molecule as this facilitates bond rupture via the formation of a Co-O-O-Co bridge. More recently [17, 18, 19, 20] Anson et al. have achieved a four-electron O_2 reduction using single metal cobalt porphyrins but with

pendant groups on the periphery of the porphyrin ring containing electrodonating $Ru(NH_3)_3^{2+}$ units. They showed that three of these groups on the periphery of the ligand were sufficient for achieving a four-electron process. Since only one single Co site is available for O_2 binding, this effect is attributed to back-bonding of d-electrons from the Ru(II) centers to the porphyrin ring and finally to the Co(II)-O_2 adduct [17, 18, 19, 20]. The same has been observed by Araki [21] for cobalt porphyrins substituted in the periphery by $Ru(bipy)_2Cl^+$ groups. All these works have been very interesting and pioneering, but the reported systems seem to lack the necessary long-term stability.

Based on the seminal work reported by Murray's group [22, 23] on the electropolymerization of metalloporphyrins, Guarr and Li [24] first reported on the electrochemical polymerization of cobalt tetra-amino phthalocyanine (CoTAPc) and the films obtained are highly electronically conductive and stable under a wide variety of conditions. Lever et al. [13] have reported that electropolymerized cobalt tetra-amino phthalocyanine (poly-CoTAPc) presents catalytic activity for the four-electron reduction of O_2 in a wide pH range (1.65–13). It has been found that these polymeric films are active for the electro-oxidation of a variety of thiols [25, 26] and that the activity of the films is not affected by their thickness. We attributed the lack of sensitivity to thickness of the catalytic activity to the fact that the films are essentially non-porous, and that the thiol molecules (2-mercaptoethanol, L-cysteine, reduced glutathione) only have access to the outermost layer of poly-CoTAPc [26]. However, their long-term stability is greatly improved.

In this work we provide for the first time a full insight into the effect of poly-CoTAPc film thickness on the catalytic activity for O_2 reduction in both alkaline and acid solution and the role of thickness in the promotion of the four-electron reduction process.

Materials and methods

All chemicals were reagent grade and were used as received except tetrabutyl-ammonium perchlorate (TBAP) (Fluka-Chemika), which was dried under vacuum at 60 °C for 3 h. Anhydrous dimethylsulfoxide (DMSO) (Baker) was thoroughly degassed with N_2 prior to use. CoTAPc was obtained from Midcentury Chemicals and used as provided. Water was deionized and purified further by double distillation. Electrolytes (NaOH, H_2SO_4) were analytical grade from Mallinckrodt.

Poly-CoTAPc films were generated by oxidative electropolymerization on a glassy carbon (GC) working electrode (Pine Instruments, exposed geometric area of 0.164 cm^2) in a DMSO + 0.1 M TBAP solution containing 1 mM CoTAPc. This was performed by cycling the working electrode potential between −0.2 V and 0.8 V at 0.2 V/s for 24, 48 and 80 cycles, as previously reported [26]. After the electropolymerization process,

the GC electrode modified with the coated film was removed from the electrolytic cell, rinsed with DMSO and finally with water. CoTAPc monomer was adsorbed on the GC electrode by placing a drop of a 1 mM of the complex in DMSO for 30 min on the surface. After this the excess of complex was removed with DMSO followed by rinsing with ethanol. A conventional three-compartment glass cell was used. A saturated calomel electrode (SCE) was employed as reference and platinum (99.99%, Aldrich) spiral wire was the auxiliary electrode. All potential values are quoted versus the SCE. Cyclic voltammetric and rotating ring-disk electrode measurements were performed with a BAS 100 Voltammetric Analyzer (Bioanalytical System) and with a AFMSRX Analytical Rotator (Pine Instruments) respectively. The collection efficiency N of the ring electrode was estimated using solutions of $Fe(CN)_6^{3-}$ and gave a value of 0.21. The electrochemical impedance measurements were made in the frequency range from 10 kHz down to 10 mHz, using an AC voltage of 5 mV amplitude at different potentials. The impedance measurements were performed using a potentiostat-galvanostat Autolab PGSTAT 30 equipment with frequency analyzer module and recording eight points per frequency decade.

Results and discussion

Figure 1 illustrates the electrochemical response of a bare GC electrode in 0.1 M TBAP/DMSO before (curve 1) and after (subsequent curves) modification with films of poly-CoTAPc obtained with various electropolymerizing scans, as indicated in Materials and methods.
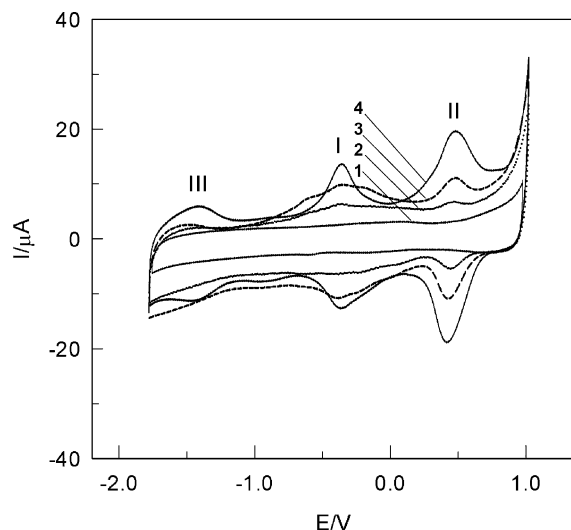

Fig. 1 Cyclic voltammograms of a glassy carbon (GC) electrode modified with poly-cobalt tetra-aminophthalocyanine (poly-CoTAPc) in a 0.1 M TBAP in DMSO solution. Scan rate: 0.2 V/s. *Curve 1* Bare GC, *curve 2* 24 electropolymerizing scans, *curve 3* 48 electropolymerizing scans, *curve 4* 80 electropolymerizing scans

a

b
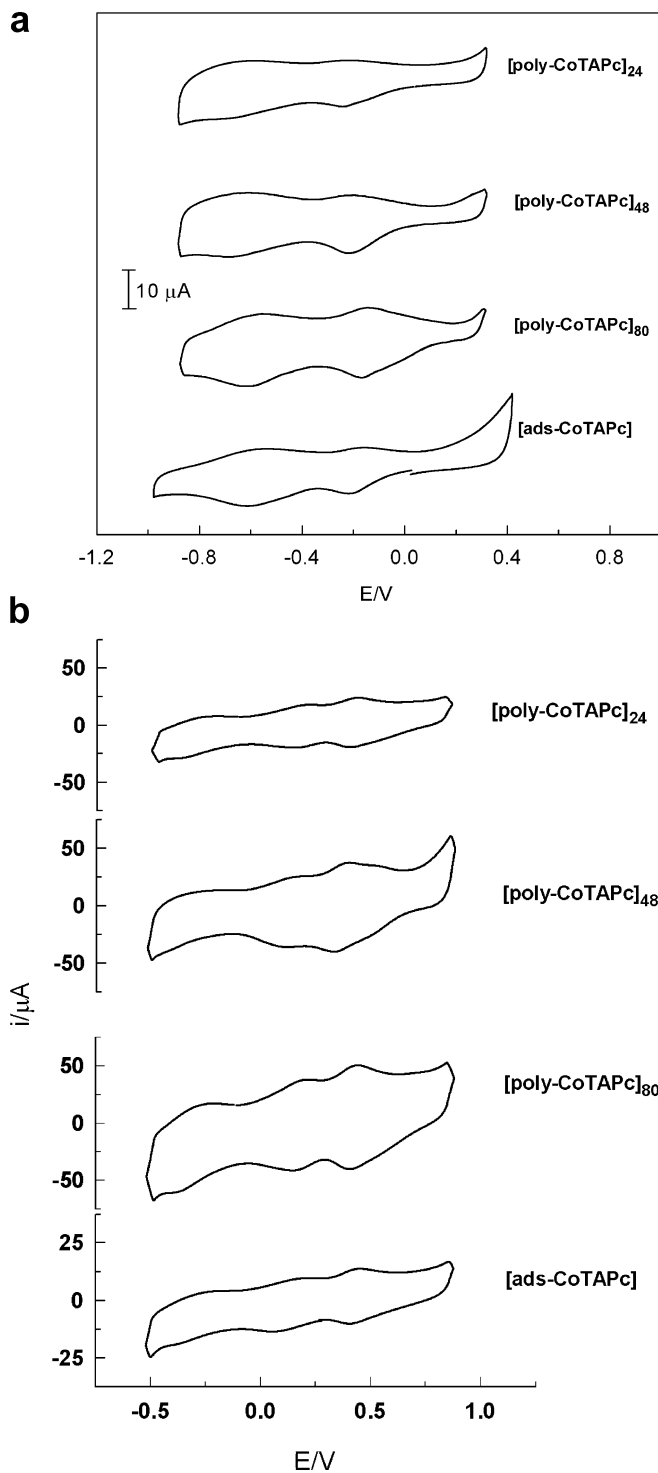
Fig. 2a, b Cyclic voltammograms of a GC electrode modified with adsorbed monomeric CoTAPc and poly-CoTAPc of different electropolymerizing scans and recorded in **a** 0.1 M NaOH, and **b** 0.05 M H_2SO_4 aqueous solution. Scan rate: 0.2 V/s

Several reversible current peaks are observed and their intensity increases with the number of electropolymerizing scans. The voltammetric response of these films is essentially similar to that observed with the monomer CoTAPc in DMSO or dimethylformamide (DMF)

a

b
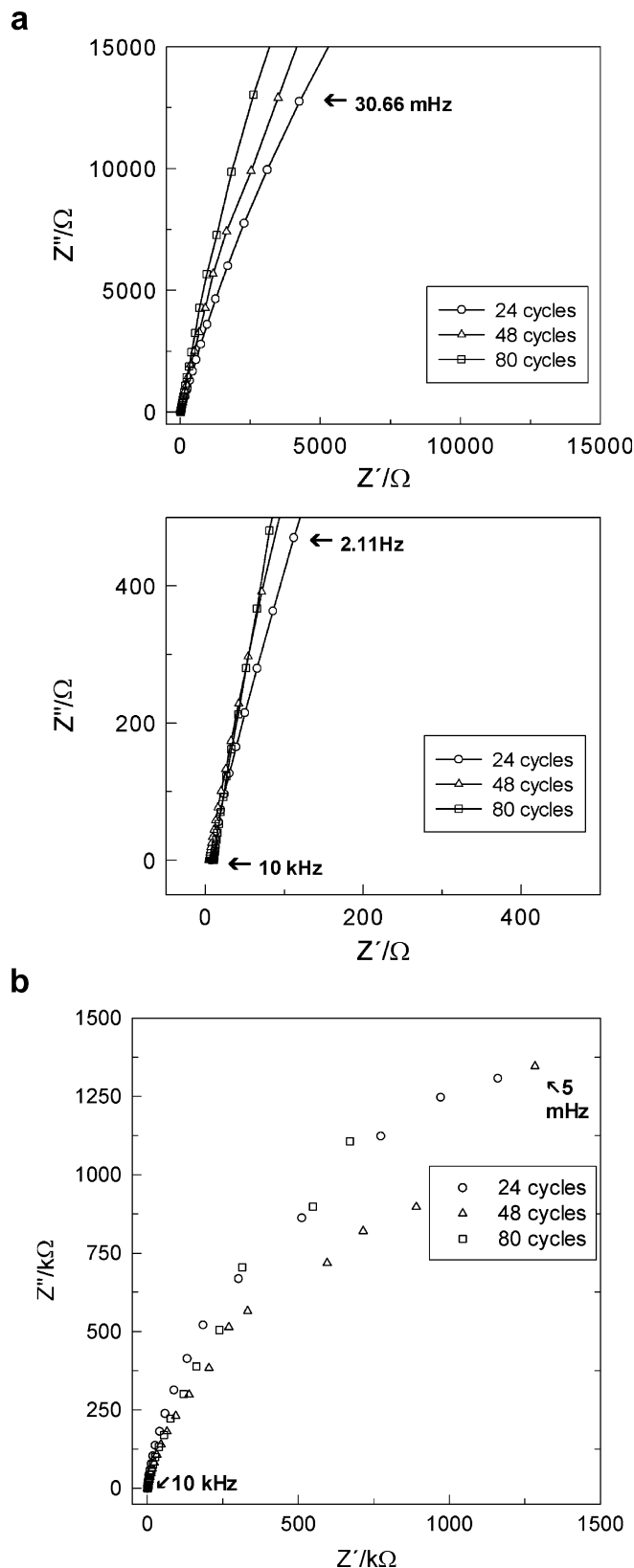
Fig. 3a, b Impedance spectra of poly-CoTAPc films, obtained with various electropolymerizing scans. Spectra recorded in **a** 0.1 M NaOH at -0.62 V, and **b** in 0.05 M H_2SO_4 aqueous solution at -0.30 V
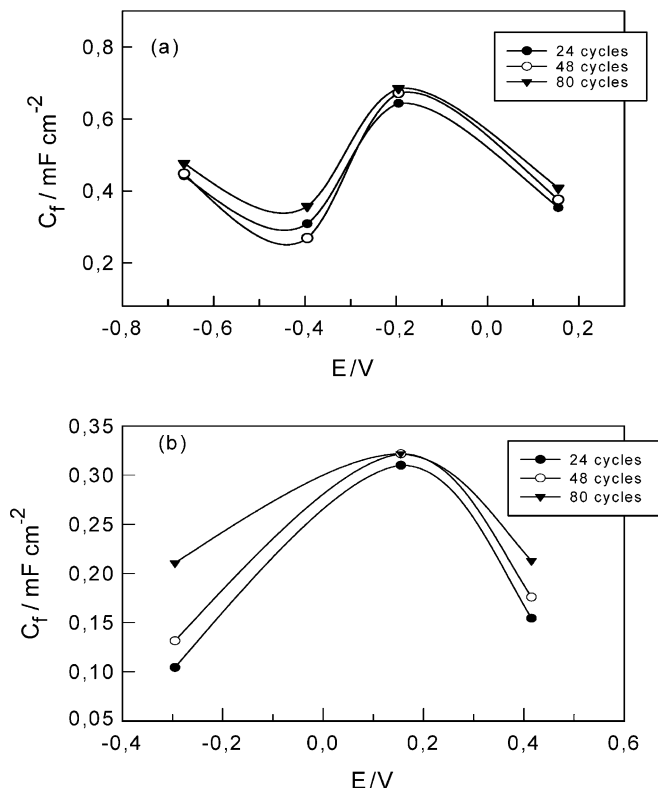
a

b
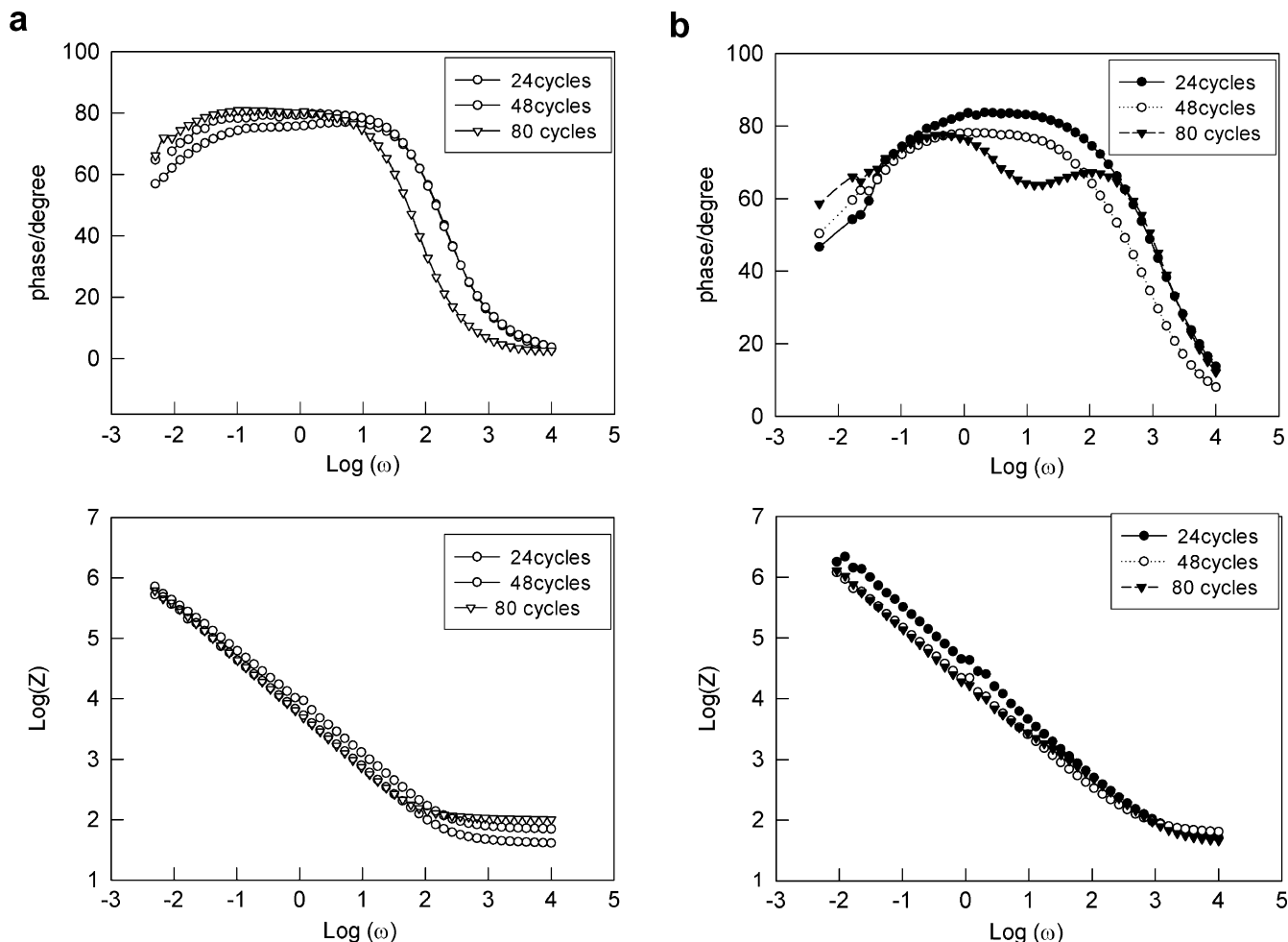
Fig. 4a, b Bode plots of poly-CoTAPc films, obtained from data in Fig. 3 with various electropolymerizing scans. a 0.1 M NaOH. b 0.05 M H_2SO_4
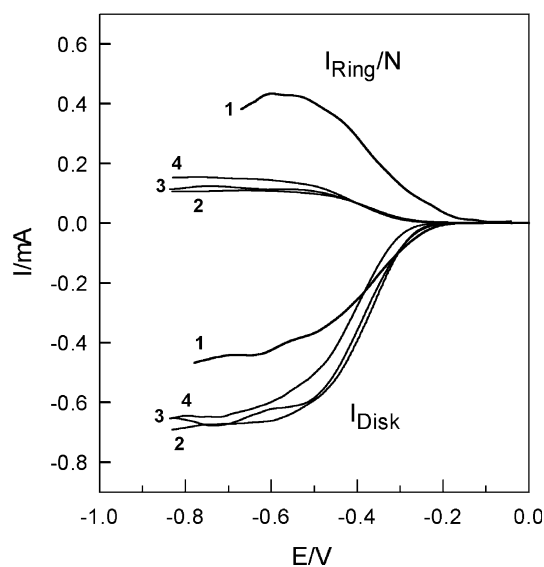
solution (not shown) [13, 24, 26]. Pairs of peaks I and II can be assigned to processes involving the Co center, i.e. Co(II)Pc(-2)/Co(I)Pc(-2) and Co(III)Pc(-2)/Co(II)Pc(-2) respectively, as previously suggested [24, 27, 28]. Pairs of peaks III are more likely to be related to a redox process involving the ligand, i.e. Co(I)Pc(-2)/Co(I)Pc(-3). Also the UV-vis spectra of poly-CoTAPc films of several thicknesses and grown on indium-tin-oxide (ITO) electrodes are similar to that obtained with monomeric CoTAPc in DMF solution as previously reported [26]. All this indicates that the essential structure of the phthalocyanine complex is not modified upon electropolymerization.

Figure 2a illustrates a series of cyclic voltammograms obtained in 0.1 M NaOH aqueous solution of GC modified with adsorbed CoTAPc and with poly-CoTAPc films of different thickness. Two redox processes can be distinguished: one at ca. −0.6 V that is attributed to the Co(II)/Co(I) reversible couple [13, 25], and another at −0.2 V which has not been assigned to a specific process [11] but probably does not involve the

Co center. This peak is not observed on other cobalt phthalocyanines with or without substituents on the periphery of the ligand [29] so it is a unique feature of CoTAPc both in monomeric or polymeric form. It can be observed from Fig. 2a that the intensity of both peaks located at ca. −0.6 V and at −0.2 V increases with film thickness. The amount of redox sites can be estimated from the charge under the peak at −0.6 V assuming that the Co(II)/(I) process involves one electron. A value of 1.01×10^{-11} mol cm^{-2} is obtained for the film of 24 cycles whereas for the film of 80 cycles a value of 2.31×10^{-11} mol cm^{-2} is obtained, which reveals some porosity of the external layers. According to a previous study [26] the film of 80 cycles is about 3.6 times thicker that the film of 24 cycles whereas the ratio of amount of redox sites is ca. 2.3. This indicates that even though as the film grows the redox response increases, a fraction of the film, probably the innermost layers of poly-CoTAPc, are electrochemically silent. Figure 2b illustrates the cyclic voltammetric behavior of the CoTAPc-based coatings in 0.05 M H_2SO_4 solution. The obtained data show that the charge under the various peaks increases a little with film thickness, illustrating once more that only the outermost film layers are electrochemically active.

Fig. 5 Faradaic capacitance of poly-CoTAPc films obtained after various electropolymerizing scans as a function of potential. **a** 0.1 M NaOH. **b** 0.05 M H_2SO_4 aqueous solution

Table 1 Percentage of H_2O_2 generated at two different potentials in 0.1 M NaOH, estimated from ring-disk data in Fig. 5

Modified electrode	% H_2O_2 $E = -0.24$ V	% H_2O_2 $E = -0.44$ V
Adsorbed CoTAPc	49	78
(Poly-CoTAPc)$_{24}$	52	40
(Poly-CoTAPc)$_{48}$	49	30
(Poly-CoTAPc)$_{80}$	32	23

films having various thicknesses (obtained with various electropolymerizing scans). The spectra were recorded in 0.1 M NaOH aqueous solution with frequencies varying between 30.66 mHz and 10 kHz at -0.62 V, which is the formal potential of the Co(II)/(I) redox process in alkaline media. At a first look on these data, it may appear that the impedance spectroscopy response is not very dependent on the film thickness: indeed, there are no zones of kinetic or diffusional control, which tends to show that the Co(II) + e $\rightarrow$ Co(I) is a fast process. So the impedance response is essentially capacitive in nature (ca. 100 μFcm^{-2}). Figure 3b illustrates the electrochemical impedance spectra of the considered poly-CoTAPc films in 0.05 M H_2SO_4 with frequencies varying between 12.4 mHz and 10 kHz, at -0.30 V, close to the formal potential of the Co(II)/(I) couple in acid solution. Again, as suggested above in alkaline media, the response is not very dependent on the film thickness.

A closer look at the electrochemical impedance measurement data reported as the Bode plots shown in Fig. 4a, b reveals a more complex behavior, depending on the frequency, the film thickness and the pH. Indeed, in acidic solution (Fig. 4b) it clearly appears that for the thickest film (prepared with 80 electropolymerizing scans) two decoupled phenomena having two different relaxation periods (ca. 3.1 and 316 Hz) contribute to the electrochemical process occurring. They could be related to different motion and/or diffusion processes within the polymer film, such as electrolyte and solvent motion, polymer chain displacements and possible proton-associated phenomena involving the polyaniline-like backbone of the film. For thin film (prepared with 24 electropolymerizing scans), both contributions appear to have closer relaxation characteristics. The film prepared with 48 electropolymerizing scans shows, obviously, an intermediate behavior. In alkaline solution, the Bode plots are less differentiated (Fig. 4a) but two phenomena are revealed. Although the exact nature of the origin of the phenomena cannot readily be determined, it clearly appears that the use of the electrochemical impedance spectroscopy allows the distinguishing of a complex behavior, in contrast to cyclic voltammetry.

Figure 5a, b depicts the faradaic capacitance [30] at low frequencies of poly-CoTAPc as a function of applied potential in both 0.1 M NaOH and 0.05 M H_2SO_4 solutions, respectively. It can be observed that the capacitance is very slightly affected by the thickness of

Fig. 6 Rotating ring-disk electrode polarization curves for O_2 reduction in 0.1 NaOH on GC coated with poly-CoTAPc of different thickness. Potential scan rate: 5 mV/s. *Curve 1* adsorbed CoTAPc, *curve 2* 80 electropolymerizing scans, *curve 3* 48 electropolymerizing scans, *curve 4* 24 electropolymerizing scans. Ring potential: 0.4 V, rotation rate: 3,600 rpm

These films were further characterized by electrochemical impedance spectroscopy. Figure 3a illustrates the electrochemical impedance spectra of poly-CoTAPc
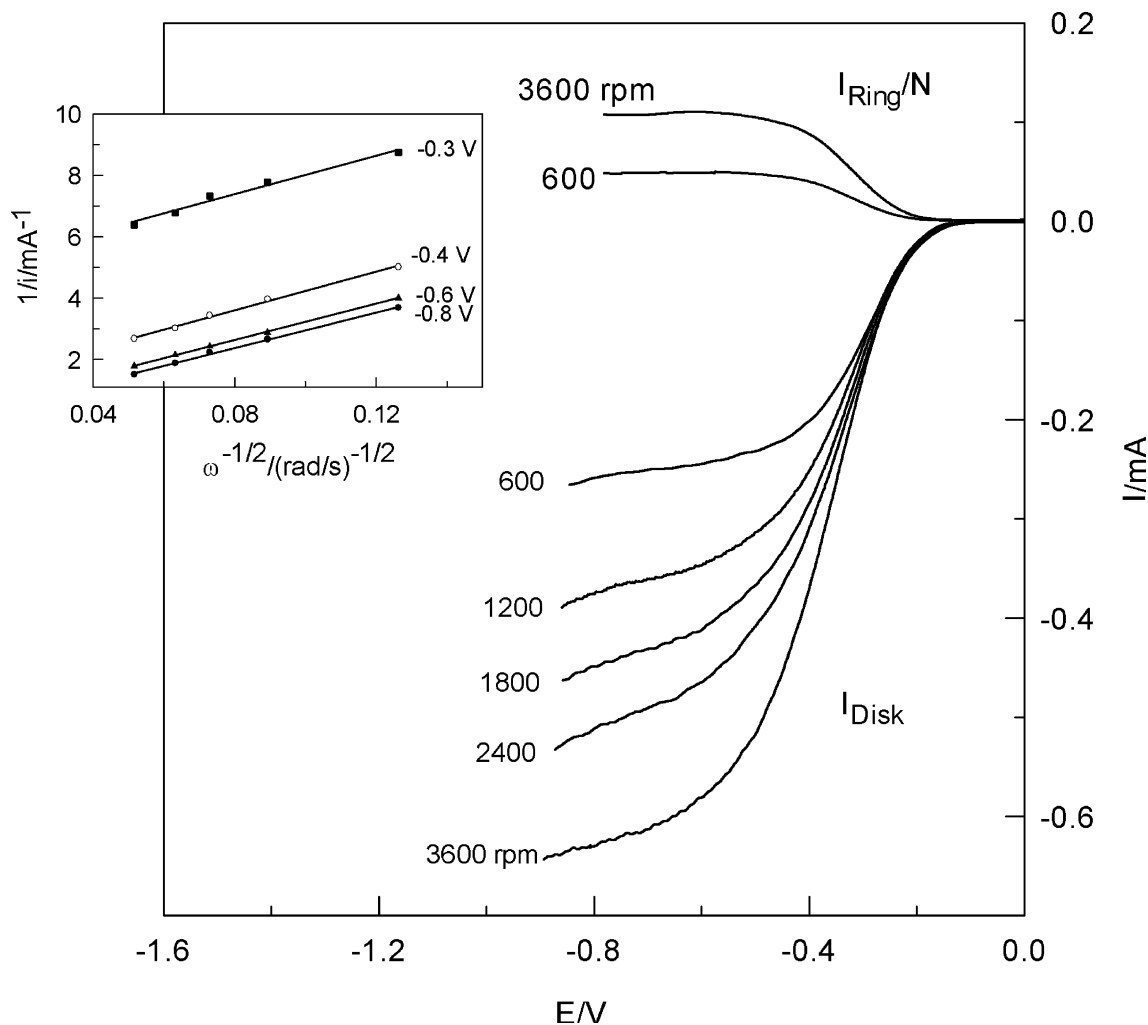
Fig. 7 Rotating disk-ring electrode data for the reduction of molecular oxygen in 0.1 M NaOH on GC modified with poly-CoTAPc of 80 electropolymerizing scans. Potential scan rate: 5 mV s^{-1}, ring potential, 0.4 V. *Insert* Koutecky-Levich plot. I_{Disk} Disk current, I_{Ring} ring current, N collection efficiency

the film. This shows that the amount of redox active sites available for charge transport within the polymer is not drastically affected by the thickness of the polymer and this suggests a low porosity for the film.

Figure 6 shows rotating ring-disk electrode data for the O$_2$ reduction in 0.1 M NaOH aqueous solution on GC coated with poly-CoTAPc of different thickness. The currents for the ring have been divided by the collection factor $N=0.21$ to facilitate the comparison between the disk and the ring currents. For example, for curve 1 obtained with adsorbed CoTAPc, the magnitude of both disk and ring currents is practically the same in all the investigated potential range. This indicates that the reduction of O$_2$ is occurring predominantly via the transfer of two electrons to give peroxide. The ring currents decrease slightly at potentials more negative than -0.6 V, which indicates that some peroxide is reduced to water or direct reduction of O$_2$ to water does

take place at those potentials. In contrast, for the electropolymerized poly-CoTAPc films of different thicknesses (curves 2–4), the ring currents are smaller than that provided with the adsorbed monomer, indicating less peroxide formation. So, a parallel four-electron O$_2$ reduction to water or reduction of peroxide to water is occurring on these films. The low yield of peroxide seems to be rather independent of the thickness of the film. So, the overall four-electron reduction of O$_2$ that is occurring in parallel with some peroxide formation is probably taking place at the poly-CoTAPc interface without the involvement of the bulk or the interior of the polymeric films. The yield in peroxide can be estimated using the following equation: %$_{peroxide} = 2 \times 100(I_R/N)/[(I_R/N) + I_D]$ where I_D and I_R are the disk and the ring currents and N is the collection efficiency. Table 1 shows the results obtained for two different potentials (data were extracted from Fig. 6).

Figure 7 shows rotating disk-ring electrode data at different rotation rates for the reduction of molecular oxygen on GC modified with thick poly-CoTAPc (prepared with 80 electropolymerizing cycles) in 0.1 M NaOH aqueous solution. For simplicity, only two rotation rates are shown for the ring data. For a process

that is first order in a diffusing reactant the disk current I is related to the rotation rate ω by the following expression: $1/I = 1/I_k + 1/B\omega^{1/2}$ [31] where I_k is the current under pure kinetic control. B is related to the diffusion limiting current as $I_L = B\omega^{1/2}$. Koutecky-Levich plots (insert) of $1/I$ versus $1/\omega^{1/2}$ for different potentials give parallel straight lines, which indicate that the reaction is first order in O_2. The reciprocal slopes B are close to 3.2×10^{-2} mA (rad s^{-1})$^{-1/2}$. The theoretical value of B, assuming $n = 4$ for the total number of electrons transferred, is 7.2×10^{-2} mA (rad s^{-1})$^{-1/2}$. The theoretical value was calculated using the Levich equation: $B = 0.20(D_{O_2})^{2/3}v^{-1/6}nF[O_2]$ from data reported in [32] where D_{O_2} is the diffusion coefficient of O_2 and v is the kinematic viscosity of the solution. So the experimentally obtained value suggests that the reaction is occurring predominantly via the transfer of two electrons to give peroxide. However the data reported in Table 1 shows that a parallel four-electron pathway for O_2 reduction does take place, since the yields in peroxide are much less than 100%.

Figure 8 shows rotating ring-disk electrode data for the O_2 reduction in 0.05 M H_2SO_4 on GC coated with poly-CoTAPc of different thicknesses. As observed in alkaline solution, the disk currents for the adsorbed CoTAPc are smaller than those observed for the polymeric poly-CoTAPc films. However, in this case the contrast is more pronounced. For example, in the case of thick poly-CoTAPc film (prepared with 80 electropolymerizing cycles), the limiting current is double that obtained on the adsorbed CoTAPc, which shows that twice as many electrons are involved in the whole O_2 reduction process. In contrast to the results obtained in alkaline media, it clearly appears that in acid media the film thickness affects the yield in peroxide (see Table 2): the thicker is the film, the less peroxide is formed. This can be easily seen on the ring currents of Fig. 9. For the thickest film, the ring currents are negligible with peroxide yields as low as 0.4% at 0.0 V. Koutecky-Levich plots (insert) of $1/I$ versus $1/\omega^{1/2}$ for different potentials give parallel straight lines which indicate that the reaction is first order in O_2. The slopes are close to 7.8×10^{-2} mA (rad s^{-1})$^{-1/2}$. The theoretical value of the slope, assuming $n = 4$ for the total number of electron transferred, is 7.2×10^{-2} mA (rad s^{-1})$^{-1/2}$. So the experimentally obtained value suggests that the reaction is occurring predominantly via the transfer of four electrons to give water. This agrees with the data reported in Table 2, which shows that the lowest yield in peroxide was obtained by the thickest film and illustrates that thicker films tend to favor a four-electron O_2 reduction mechanism to give water versus a two-electron O_2 reduction mechanism to give peroxide.

Figure 10 shows the Tafel plots obtained for O_2 reduction in 0.1 M NaOH on the GC electrode modified with adsorbed and electropolymerized poly-CoTAPc films of different thicknesses (data are extracted from Fig. 6). The slopes range from -0.046 to -0.059 V/decade, which suggests that in all cases a fast electron-
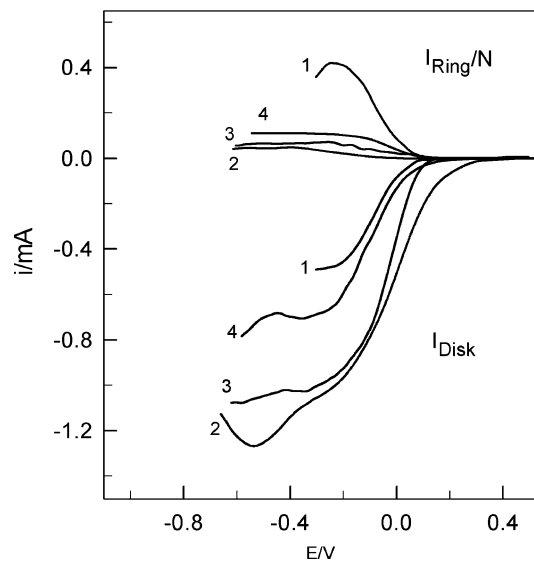

Fig. 8 Rotating ring-disk electrode polarization curves for O_2 reduction in 0.05 H_2SO_4 on GC coated with poly-CoTAPc of different thicknesses and with an adsorbed monomeric CoTAPc layer. Potential scan rate: 5 mV/s. *Curve 1* Adsorbed CoTAPc, *curve 2* 80 electropolymerizing scans, *curve 3* 48 electropolymerizing scans, *curve 4* 24 electropolymerizing scans. Ring potential: 0.4 V, rotation rate: 3,600 rpm

Table 2 % H_2O_2 generated at two different potentials, in 0.1 M H_2SO_4 estimated from ring-disk data in Fig. 7

| Modified electrode	% H_2O_2 $E = 0.0$ V	% H_2O_2 $E = -0.25$ V
Adsorbed CoTAPc	98	93
(Poly-CoTAPc)$_{24}$	46	28
(Poly-CoTAPc)$_{48}$	12	14
(Poly-CoTAPc)$_{80}$	0.4	5

transfer step is followed by a slow chemical step. The Tafel plots obtained for O_2 reduction in 0.05 M H_2SO_4 are reported in Fig. 11 (data are extracted from Fig. 8). The slopes are close to -0.16 V/decade for the adsorbed CoTAPc and the thinnest electropolymerized poly-CoTAPc film. For thicker poly-CoTAPc films, the slopes change to values of -0.048 and -0.059 V/decade, suggesting that the electron transfer mechanism is different. Slopes of -0.16 V/decade point to a first electron transfer step as rate determining, whereas the lower slopes for thicker films suggest a fast electron-transfer step is followed by a slow chemical step.

In summary of the above reported observations, we may say that in the case of CoTAPc, the increase in catalytic activity for the four-electron reduction of O_2 upon electropolymerization is real in acid solution, but its origin is not clear yet. It may be possible that molecular oxygen binds to two Co centers simultaneously in the polymeric matrix in a fashion similar to that observed with cobalt face-to-face porphyrins, as reported by Anson and Collman [14, 15, 16]. However, it
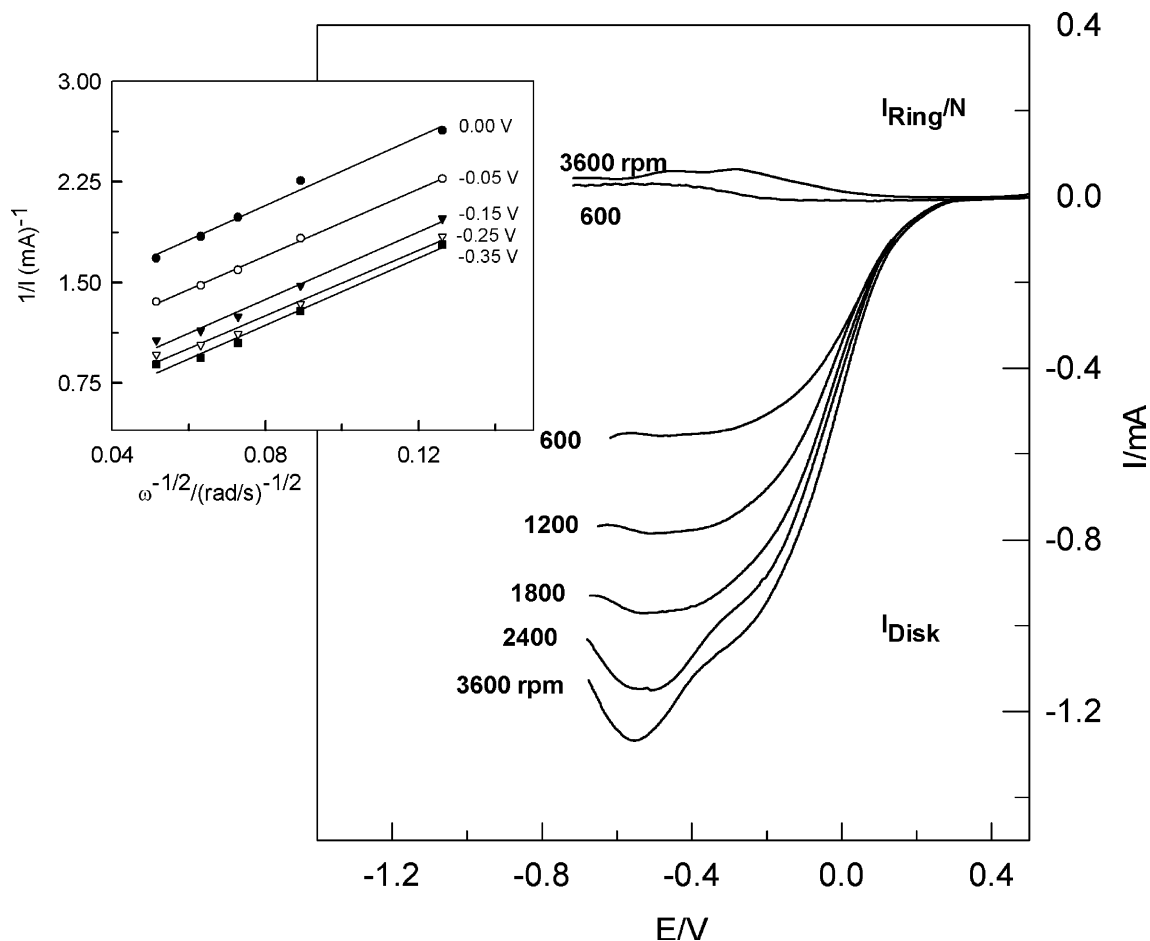
Fig. 9 Rotating disk-ring electrode data for the reduction of molecular oxygen in 0.05 M H_2SO_4 on GC modified with poly-CoTAPc of 80 electropolymerizing scans. Potential scan rate: 5 mV s^{-1}, ring potential: 0.4 V. *Insert* Koutecky-Levich plot

is unlikely that the ideal separation of 4 Å between the two Co centers is achieved simply by electropolymerization and tangling of the polymeric chains. In the case of cobalt porphyrins bearing electron-donating metal complexes on the periphery of the macrocycle, the mechanistic basis of the conversion of the two-electron to four-electron electrocatalysts is believed to depend upon back-bonding between the coordinated metal through the pendant substituent to the porphyrin ring [17, 18, 19, 20]. It is possible, then, that upon electropolymerization, CoTAPc becomes substituted on the periphery of the macrocycle, where amino groups are initially located, probably randomly, but these peripheral groups (which are also CoTAPc units) back bond to the phthalocyanine ring and then to the Co center, increasing in this fashion the activity of these centers for the four-electron reduction of molecular oxygen. It is interesting to notice at this point that we have recently shown that monomeric FeTAPc promotes, at low overpotentials, the four-electron reduction of O_2 in alkaline media whereas polymeric poly-FeTAPc only promotes the two-electron reduction [33]. So, FeTAPc
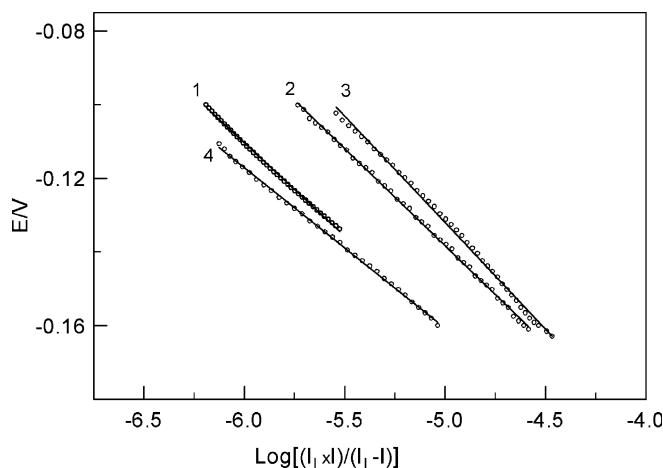
Fig. 10 Tafel plots obtained for O_2 reduction in 0.1 M NaOH on GC electrode modified with adsorbed CoTAPc (*curve 1*) and poly-CoTAPc of different thicknesses (*curve 2* 80 electropolymerizing scans, *curve 3* 48 electropolymerizing scans, *curve 4* 24 electropolymerizing scans. Data extracted from Fig. 6)

behaves in the opposite way to CoTAPc, suggesting that the change in mechanism from two to four electrons for poly-CoTAPc is more related to electronic factors than to steric or geometric factors.
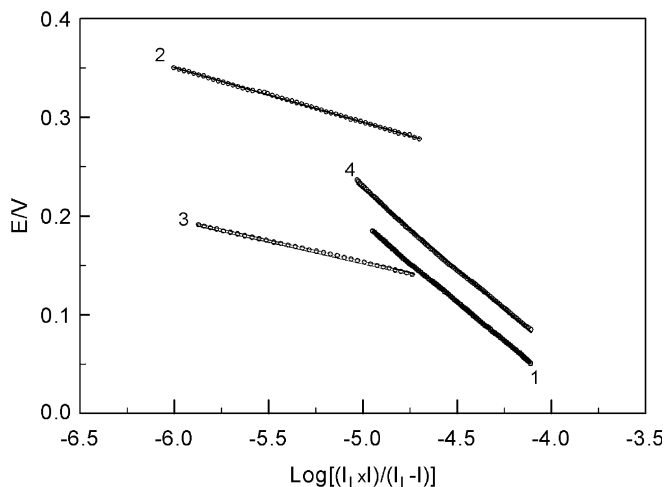
Fig. 11 Tafel plots for O_2 reduction in 0.05 M H_2SO_4 on GC electrode modified with adsorbed CoTAPc (*curve 1*) and poly-CoTAPc of different thickness (*curve 2* 80 electropolymerizing scans, *curve 3* 48 electropolymerizing scans, *curve 4* 24 electropolymerizing scans. Data extracted from Fig. 8)

Conclusions

Polymeric poly-CoTAPc films of various thicknesses have been characterized by electrochemical impedance spectroscopy and it appears that in basic media the types of phenomena revealed to be occurring depend less on the film thickness than in acid. For O_2 reduction, the results showed that poly-CoTAPc is more active than the monomeric CoTAPc adsorbed on GC. Indeed, rotating ring-disk electrode data showed that polymeric CoTAPc promotes the four-electron reduction of O_2 to water, in parallel to a two-electron reduction to give peroxide. On monomeric and thin films of poly-Co-TAPc, a two-electron reduction mechanism predominates. In basic media the activity increases slightly with thickness whereas in acid media this is more pronounced and this agrees with the presence of more redox sites in thicker films, which seem to be more accessible in acid. This parallels the observed behavior revealed by electrochemical impedance spectroscopy that showed dual phenomena with different relaxation periods in acid media. Also, it appears from this work that in alkaline media, the Tafel slopes for O_2 reduction are not far from a theoretical value of -0.059 V/decade, which is the typical Tafel slope for a slow chemical step preceded by a fast one-electron transfer step. In acid, however, theses slopes are only observed for rather thick poly-CoTAPc films. For adsorbed CoTAPc and thin poly-CoTAPc, slopes are -0.16 V/decade. So in acid, low Tafel slopes are associated with low yields in peroxide and high Tafel slopes are associated with high yields in peroxide. In acid then, the electron transfer mechanism is related to the over whole reaction pathway of O_2 reduction, to give peroxide or water as the final product of the reaction.

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