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Study of the deposition and characterisation of a 5,10,15,20-tetrakis-(4-sulphonatophenyl)porphyrin Co(II) layer at gold surfaces in alkaline solution

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Abstract

In this paper, the electrodeposition of Co(II)TSPor at gold electrodes is described. It was found that this deposition is initially controlled by kinetic parameters leading to a nearly 100% coverage of the electrode surface. However, once formed a reorganisation of the layer occurs. Experimental evidence that Co(II)TSPor is deposited was provided by using Raman spectroscopy. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

Porphyrins are widespread compounds in nature. Natural colours are often related to porphyrins. They are important for several mechanisms in life: they catalyse enzymatic reactions and are, for instance, responsible for the oxygen transport in the human body [1]. Phthalocyanines, frequently used molecules in electrocatalysis [2–5], are closely related to these naturally occurring porphyrins. The basic structure of porphyrin consists of four pyrrole units which are linked by four methine bridges. The porphyrin macrocycle is geometrically flat and has an conjugated 18 π -electron system. Following Hückel's rule, the porphyrin ring can be considered as an aromatic system. The possibility of delocalization

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of the electrons is important for its chemical activity and biological functions. The porphyrin ring is very stable towards concentrated acids and bases. Its major characteristics are its thermal and chemical stability, coupled with its extensive redox chemistry.

The aromatic ring structure can be electrochemically oxidised and/or reduced. More than 70 different metal ions can form a complex by coordinating with the porphyrin ring. When the central metal is a transition metal, its ion can also be oxidised and/or reduced. The solubility of the porphyrin in an aqueous solution can be efficiently altered by substitution of sulfonatophenyl groups [6,7].

In this paper, the electrochemical behavior of 5,10,15,20tetrakis-(4-sulphonatophenyl) porphyrin Co(II), tetrasodium salt (CoTSPor, Fig. 1) at a gold electrode in alkaline solution is described. The immobilization of CoTSPor on a gold electrode can lead to a modified electrode with electrocatalytic properties [8]. Cobalt(II) was selected based on its well-known redox behaviour and electrocatalytic properties.

Electrodeposition is the method used in this study to deposit a film of CoTSPor onto a gold electrode. A continuous

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Fig. 1. Molecular structure of 5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin cobalt(II), tetrasodium salt.

potential cycling of the electrode between two potentials in a CoTSPor solution can lead to a modification of the bare electrode. By measuring the current, it is possible to follow the adsorption process in situ.

Characterisation of the modified electrodes is done by electrochemical and spectroscopic methods, including Raman spectroscopy.

2. Experimental

A saturated calomel reference electrode (SCE) with two compartments (radiometer) and a carbon counter electrode were used. The working electrodes were gold electrodes with a diameter of 1.6 mm (purity 99.95%, BAS, England) and were pretreated by mechanical and electrochemical polishing. Before its first use, the electrode surface was scoured briefly on SiC-emery paper 1200 grit to obtain a fresh surface. To smoothen this relatively rough surface, it was further subjected to sequential polishing on a polishing cloth covered with alumina (Buehler) powder of 1, 0.3 and 0.05 µm particle size for respectively 5, 10 and 20 min. To remove any adherent Al₂O₃ particles, the electrode surface was rinsed thoroughly with doubly deionised water and cleaned in an ultrasonic bath (Branson 3210) for 2 min. Finally, the electrode was pretreated electrochemically by scanning it in a buffer solution, pH 12, between -1.2 and 0.6 V versus SCE until five subsequent scans were identical. The scan rate for all cyclic voltammetric experiments was $50 \,\mathrm{mV}\,\mathrm{s}^{-1}$.

A PGSTAT20 potentiostat (ECO Chemie, the Netherlands) controlled by GPES 4.9 software package running on a Pentium II computer (Eknadata) was used to record the voltammetric curves. Measurement of the pH of the solution was done with a Orion Benchtop pH-meter model 420A. The CoTSPor sodium salt (purity 98%) was purchased from Porphyrin Systems (Lübeck, Germany). The buffer solution of pH 12 (Na₂HPO₄/NaOH) and sodium dithionite were purchased from Riedel-de Haën (Belgium). Before each experiment, pure nitrogen was bubbled through the cell solution for 20 min.

Raman analysis of the modified electrodes has been performed on a Rensihaw system-1000 spectrometer (Renishaw, Wotton Under Edge, UK). Electrodes were mounted on the microscope table and the laser light (780 nm, ca. 5 mW at the sample) was focussed directly on the electrode surface by using an Olympus 50X objective, obtaining a spot size of ca. 2 μ m diameter. The backscattered radiation was collected by the same objective lens and the Rayleigh line was suppressed by a notch filter. The light was dispersed over a 1200 lines/mm diffraction grating and was collected on a Peltier cooled charge coupled device (CCD) detector. Spectra were recorded in the Stokes branch of the spectrum, between 300 and 1700 cm⁻¹.

3. Results and discussion

The first 19 cyclic voltammetric scans recorded at a gold electrode in a pH 12 buffer solution (curve 1) and a



Fig. 2. Current–potential curves recorded at a gold disc electrode in a pH 12 buffer solution in the absence (curve 1, dotted line) and presence (curves 2–7) of 8.04×10^{-3} mol L⁻¹ Co(II)TSPor at a scan rate of 50 mV s⁻¹ and a temperature of 298.0 K as a function of scan number. Scan numbers are: (2) 1; (3) 2; (4) 6; (5) 10; (6) 14 and (7) 19. Inset: enlarged view of the –1 to –0.2 V potential region.

buffer solution containing 8.04×10^{-3} mol L⁻¹ Co(II)TSPor (curves 2–7) are shown in Fig. 2. The voltammetric behaviour is similar, but not identical, to the behaviour of a gold electrode in a CoTSPc (cobalt(II) tetrasulphonated phthalocyanine sodium salt) solution [9]. In what follows, the differences between both molecules concerning their electrochemistry will be explained. The peaks, corresponding to the oxidation of the gold surface (A_a) and the reduction of the gold oxide formed during surface oxidation (A_c), decrease markedly during the first 19 scans when cycled in a CoTSPor solution. This is a first indication of adsorption of CoTSPor onto the gold electrode, as covering the gold surface with CoTSPor prevents its oxidation and reduction.

In curves 2–7, it can be seen that three new oxidation peaks, at about 0.3 V (B_a), -0.9 V (C_a) and -0.8 V (D_a) versus SCE, and three new reduction waves, at about -0.4 V (B_c) , $-0.8 V (C_c)$ and $-1 V (D_c)$ versus SCE, occur. The mentioned values of the peak potential of processes Cc and Dc are only valid for the first scan because their peak maximum shifts towards more negative potentials with increasing scan number. The decrease of oxidation peak Ca and the increase of oxidation peak Ba and reduction peaks Bc and Cc continue until scan 19. Process D_a appears from scan 10 and its peak height increases from scan 10 until scan 19. The peak maximum of D_c shifts towards more negative potentials in the first 10 scans, which suggests that the completed shift of peak potential of peak D_c initiates the appearance of peak D_a. Continuation of the scanning beyond scan 19 results in a different behaviour (Fig. 3).

Fig. 3 shows curves obtained after scan 19, from scan 19 (curve 1) to scan 100 (curve 4). It is remarkable that oxidation



Fig. 3. Current–potential curves recorded at a gold disc electrode in a pH 12 buffer solution containing 8.04×10^{-3} mol L⁻¹ Co(II)TSPor at a scan rate of 50 mV s⁻¹ and a temperature of 298.0 K as a function of scan number. Scan numbers are: (1) 19; (2) 50; (3) 80 and (4) 100.

peak B_a and both reduction peaks B_c and A_c stabilise after scan 19. Processes C and D reverse in their increasing or declining behaviour. After scan 19, peak currents of C_a and C_c increase, while the peaks of wave D_a and D_c decrease. Similar to the CoTSPc study [9], scan 19 can be considered as the scan of maximum coverage. Before scan 19, peaks C_a and C_c , as well as processes D_a and D_c , can be attributed to the ring reduction and oxidation of CoTSPor in solution.

It is also important to note that the rate of decrease of peak A_c is different from the rate of increase of process B_c . Fig. 4 shows the relationship between the charge of processes A_c and B_c and the scan number. Two different slopes (A_c) indicates the convolution of two processes, one increasing in time (adsorption), one decreasing in time (gold oxide reduction). This is rather clear because process A_c is the result of more



Fig. 4. Relationship between charge of processes $B_{\rm c}$ and $A_{\rm c}$ and scan number.

than one reaction. The peak current decreases due to covering of the gold surface and increases due to electroactive properties of deposited Co(II)TSPor at the same potential (ring reduction of adsorbed CoTSPor).

For scan 19, the charge related to oxidation wave B_a and the charge related to the reduction waves B_{c} and A_{c} is almost the same and equal to $3.2 \pm 0.5 \,\mu$ C. Fig. 4 shows that the charges of B_c and A_c are equal. Therefore, it is supposed that process A_c after scan 19 is only due to the reduction of the adsorbed fraction of CoTSPor, which means that at scan 19, a maximum value for the surface coverage is obtained. No more gold can be oxidized (Aa) or no more gold oxides can be reduced (A_c). At the potential of process, A_c only the ring reduction of adsorbed CoTSPor takes place at scan 19. The increase with scan number of peaks B_a and B_c is due to the deposition of Co(II)TSPor at the gold surface that grows with scan number until scan 19. Process A is, before scan 19, related to the gold reaction and a CoTSPor adsorption reaction. After scan 19, process A can be explained as an adsorption reaction of CoTSPor. No gold related processes occur because at scan 19 all gold is covered with CoTSPor.

In correlation with the data found in literature [9–11], peaks B_a and B_c are attributed to the Co(III)TSPor_{ads}/Co(II)TSPor_{ads} redox system. Fig. 5 represents the voltammetric behaviour of a CoTSPor modified electrode in a pH 12 buffer solution. Only the adsorption processes are now



Fig. 5. Current–potential curve of scan 2 of a continuous cyclic voltammetric scanning experiment recorded at a gold electrode modified with CoTSPor in a pH 12 buffer solution.

present in the figure. Processes Bc and Ba stand for the reduction and oxidation of the $Co(III)_{ads}/Co(II)_{ads}$ redox system. Because of the considerable difference in peak potential, this process can be classified as irreversible. The charge under the peaks for these processes as well as the charge associated with peak A_c is equal to $3.2 \pm 0.5 \,\mu\text{C}$. Knowing that the charge of one electron is 1.6×10^{-19} C it follows that about 2.0×10^{13} electrons are exchanged in each reaction. This leads to the conclusion that $0.97 \times 10^{15} \text{ mol } \text{L}^{-1}$ CoT-SPor or 1.61×10^{-9} mol L⁻¹ CoTSPor is deposited on 1 cm² of gold surface. Supposing the formation of a monolayer, each CoTSPor molecule would cover 0.1 nm². Nevertheless, a CoTSPor molecule deposited in a flat configuration is expected to cover about 2 nm². This means that Co(II)TSPor is adsorbed perpendicularly and/or a multilayer is formed. However, the changes in the peaks as a function of scan number observed in Figs. 2 and 3 indicate that a mixture of flat and perpendicular orientation of the molecules is obtained. The process before scan 19 is kinetically controlled, explaining the chaotic orientation of the CoTSPor molecules. In the CoTSPc study, it was seen that the situation changed considerably after the maximum coverage was obtained. In the case of CoTSPor, only small differences are observed after scan 19 (Fig. 3). The changes observed after the maximum coverage was reached in the case of CoTSPc were explained as the reorganisation of the deposited layer to form, from a thermodynamic point of view, a more stable layer consisting of columnar aggregates [8]. The CoTSPor molecules are not able to create such columnar aggregates because of the free benzyl groups on the porphyrin ring. These groups are perpendicularly oriented on the ring, which prevents the CoTSPor molecules to stick together and explains the slow evolution after that the maximum coverage was obtained.

Finally, processes D_c and D_a can be explained as the catalytic ring reduction and oxidation of CoTSPor in solution on a chaotic multilayer of CoTSPor molecules. Processes C_c and C_a can be interpreted as the ring reduction and oxidation on a less chaotic oriented CoTSPor multilayer. Electrochemical measurements of TSPor without Co also show a reduction wave at these potentials. The slow evolution of these last two peaks after the breaking point can be explained by the disability of the CoTSPor molecules to form a closely packed multilayer.

3.1. Scan rate study

The influence of the scan rate (ν) on the peak current (I_p) is investigated to find out whether the reactions attributed to the peaks observed in Figs. 2 and 3 are due to adsorption or to a diffusion controlled process. A slope of the relationship between log I_p and log ν equal to 1 would correspond to oxidation or reduction of CoTSPor adsorbed at the gold electrode, while a slope of 0.5 rather indicates a rate determining diffusion of CoTSPor or another species, such as hydroxide ions, towards the electrode surface [12–14]. Fig. 6 shows the relationship between log I_p and log ν for the different peaks



Fig. 6. Logarithmic plot of the peak current of the peaks observed in Figs. 2 and 3 as a function of scan rate. Curve: (1) peak B_c , (2) peak A_c , (3) peak B_a , (4) peak D_c and (5) peak D_a .

observed. Peaks D_a and D_c can be considered as resulting from diffusion controlled reactions because of the log I_p versus log ν slope value of 0.5 (0.494 and 0.502). Variation of the CoTSPor concentration, while the concentration of the other compounds in solution was kept constant, showed that these peaks are due to diffusion of Co(II)TSPor towards the electrode surface and not to another compound because of the linear relationshiop obtained between peak current and Co(II)TSPor concentration. The other processes are due to adsorption reactions with a value of 1 for the log I_p versus log ν slope (B_c, 1.048; A_c, 0.870 and B_a, 0.987).

3.2. Concentration study

Similar results were obtained when the same experiments as above were done for other CoTSPor concentrations. The same peaks were observed, only the scan corresponding with a maximum coverage was different for each concentration. A concentration of $8.04 \text{ mmol } \text{L}^{-1}$ CoTSPor needs 19 scans to reach the break in the trend of the behaviour, corresponding to a maximum coverage of the electrode surface. A concentration of $5.92 \text{ mmol } L^{-1}$ CoTSPor demands 42 scans, 3.95 mmol L^{-1} CoTSPor demands 59 scans and $1.97 \text{ mmol } \text{L}^{-1}$ CoTSPor demands 82 scans. The smaller the concentration of CoTSPor, the longer it takes to reach the point of maximum coverage. This is expected because more CoTSPor in solution means more of it is transported towards the electrode surface per time unit. The relationship between the number of scans to reach the maximum coverage and the concentration CoTSPor is linear.

3.3. Characterisation of the CoTSPor layer

Fig. 6 already provides evidence of the occurrence of adsorption associated with several peaks based on electrochemical experiments. Raman measurements were used to give further experimental evidence of the formation of an adsorbed CoTSPor layer at a gold electrode by cycling the electrode potential in a CoTSPor solution. The vibrations



Fig. 7. Raman spectra obtained for Co(II)TSPor deposited at the surface of a gold electrode in alkaline solution.

seen in the Raman spectra are characteristic for those of a CoTSPor molecule. In addition, the Raman band positions and bandwidth are similar to those of pure crystalline substances (1528, 1451, 748 and 681 cm^{-1}) [15–16]. Spectra of the CoTSPor particles are shown in Fig. 7. When studying the modified electrodes after rinsing with pH 12 buffer solution, it was hard to see a layer on the electrode surface, but small crystals could be found. When recording a spectrum of these grains, porphyrin spectra were obtained. These spectra were less intense than the corresponding spectra of the unrinsed electrodes are broader. This may be related to a lower degree of crystallinity after rinsing.

4. Conclusion

The hypothesis regarding the electrodeposition of CoT-SPor on a gold electrode, described in this paper, is based on the electrochemical observations made while following the current-potential behaviour as a function of scan number and CoTSPor concentration. Peaks due to the Co(III)TSPorads/Co(II)TSPorads redox system were identified as well as peaks due to ring oxidation and reduction of CoTSPor in solution. The deposition is controlled by kinetics before the breaking point, which is the point of maximum adsorption, resulting in a chaotic multilayer of CoTSPor molecules. After the breaking point, a slow reorganisation of the chaotic multilayer occurs. The axially coordinated benzyl groups are responsible for the slowness of this process. A study of the deposited layer with spectroscopic methods, such as Raman spectroscopy, gives the ultimate proof of adsorption of the porphyrin.

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