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Sulfide Ion Electrooxidation Catalysed by Cobalt Phthalocyanine Microcrystals

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Abstract. Electrooxidation of sulfide ion catalysed by microcrystals of cobalt phthalocyanine was investigated by cyclic voltammetry in 0.5 *M* KNO_3 at pH 9.22. Traces of catalyst were immobilized at the surface of a paraffin-impregnated graphite electrode by the mechanical transfer of its powder. The electrooxidation of HS^- proceeds in two irreversible steps, with the first peak between 0 V and −0.12 V and the second at 0.17 V. The first step is second order in HS^- and its product is the adsorbed disulfide, which may further dissociate to give adsorbed sulfur atoms. The reduction of sulfur occurs at −0.1 V.

Key words: sulfide, electrooxidation, cobalt phthalocyanine, cyclic voltammetry.

Abrasive stripping voltammetry (AbrSV) is a new microanalytical technique for the electrochemical study of solid compounds [1–3]. It is based on the mechanical transfer of microparticles to an electrode surface. In a previous paper [4] it was demonstrated that the method can be used for the direct electrochemical characterization of cobalt phthalocyanine powder. It was shown that the electroreduction of oxygen can be catalysed by traces of this pigment. These investigations were extended to the catalytic electrooxidation of sulfide ion and its mechanism. The oxidation of hydrogen sulfide is a very slow and totally irreversible electrode process [5–8]. Its products are sulfur and polysulfides, depending on the experimental conditions. On graphite electrodes, the oxidation develops at potentials more positive than 0 V vs SCE giving a poorly defined voltammetric response. The reduction of sulfur occurs at −0.7 V vs SCE. Electrooxidation of mercaptans is also kinetically controlled and followed by irreversible dimerization [9–12]. Cysteine is oxidized to cystine at 0.6 V [9, 12], while cystine is reduced back to cysteine at −0.9 V [10]. Cobalt phthalocyanine [Co(II)Pc] is a well-known catalyst for the oxidation of hydrogen sulfide [13–15], cysteine [16–19], glutathione [18], mercaptoethanol [20], NADH [21], thiopurine [22], oxalic acid [23], and hydroxylamine [24], and for the reduction of oxygen [25, 26]. For electrocatalytic purposes, Co(II)Pc is either incorporated in a carbon paste electrode [18, 22], or immobilized at an electrode surface by adsorption [17, 20, 25], electrodeposition [14] or electropolymerisation [15, 19, 21, 23, 24, 26]. The catalytic effects of Co(II)Pc are interpreted by mechanisms based on the formation of a complex between the substrate and the catalyst [16]. The transfer of electrons is supposed to occur in the coordination sphere of the complex. Thio-compounds are linked to Co(II)Pc through the sulfur atom.

Experimental

Analytical grade KNO_3 and Na_2S (both Merck), cobalt phthalocyanine ($C_{32}H_{16}N_8Co$) (Fluka) and a standard buffer solution pH 9.22 (H_3BO_3/NaOH/KCl) (Merck) were used as received. Water was doubly distilled. Fresh stock solutions of 10^{-2}*M* Na_2S were prepared daily with deoxygenated water. Electrolytic solutions were buffered to pH 9.22 by adding 1 mL of the standard buffer solution to 9 mL of the supporting electrolyte. At pH 9.2 the dominant ionic species of sulfide is HS^- [6].

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The experiments were performed with a spectral-grade-purity paraffin-impregnated graphite rod as the working electrode, used in conjunction with a platinum gauze counter-electrode and a Ag/AgCl/3*M* KCl (Methrohm) reference electrode. Before each voltammetric measurement, a circular surface of the graphite rod was rinsed with distilled water, polished on a wet polishing cloth, rinsed again, dried with a fine-grade paper tissue and carefully polished on a dry, white paper sheet. Then it was pressed into the metallophthalocyanine powder on a highly glazed ceramic tile and moved in a circular pattern for about 10 s [2, 3]. By this procedure, the surface is contaminated by traces of pigment and can be used as a modified working electrode. The area of the electrode surface was 0.785 cm^2.

Voltammetric measurements were performed by using a multimode polarograph Autolab (EcoChemie, Utrecht) which was connected to an AT-286 personal computer and a printer.

Solutions were degassed with high-purity nitrogen for 30 min prior to the addition of Na_2S solution. A nitrogen blanket was maintained thereafter. The cell was thermostated at 20 °C.

Results and Discussion

Cyclic voltammograms (CV) of Co(II)Pc particles which had been abrasively transferred to the surface of a paraffin-impregnated graphite electrode (PIGE) in 1 *M* KNO_3 buffered at pH 9.22 are shown in Fig. 1. They are dominated by oxidation peaks at 1.125 V vs Ag/AgCl/3 *M* KCl, which can be attributed to the redox reaction of organic parts of the phthalocyanine molecule [27]. The rest of the response consists of four main peaks: an oxidative one at 0.86 V, reductive ones at 0.55 V and −0.75 V and a re-oxidative peak at −0.36 V. They can be associated with two redox reactions in which the charges can be either localized at the metal centre, or delocalized in the aromatic structure of the macromolecule [14, 17, 18, 24, 25, 27–30]:

$$\mathrm{Co(II)Pc/Co(III)Pc^{+}NO_3^{-}} \text{ or } \mathrm{Co(II)Pc/Co(II)Pc^{+}NO_3^{-}} \quad (\bar{E} = 0.71\ V)$$

$$\mathrm{Co(II)Pc/Co(I)Pc^{-}K^{+}} \text{ or } \mathrm{Co(II)Pc/Co(II)Pc^{-}K^{+}} \quad (\bar{E} = -0.55\ V)$$

Here it is important to note that Co(II)Pc is least electroactive between −0.2 V and +0.3 V. This general response does not change upon the addition of 1×10^{-3} *M* Na_2S, because its oxidation gives a hundred times smaller current.

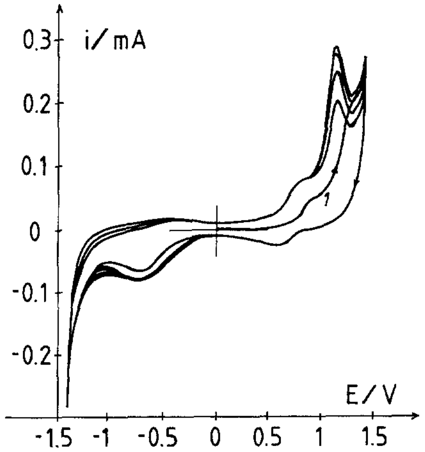

Fig. 1. Cyclic voltammograms of mechanically transferred microcrystals of cobalt phthalocyanine on a paraffin-impregnated graphite electrode (Co(II)Pc/PIGE) in 1 *M* KNO_3 buffered at pH 9.22. $E_{st} = 0$ V, $v = 100$ mV/s. The first scan is marked

The faradaic conductivity of cobalt phthalocyanine microcrystals immobilized on the graphite electrode surface, as well as of its vapour-deposited film, can be explained by an electron self-exchange mechanism which is accompanied by the simultaneous inclusion or expulsion of electrolyte ions into or from the crystal structure [4, 28, 31–33]. This exchange of ions can be a rate-determining step of redox reactions. If the electrode potential is changed by cycling in a wide range between 1.5 V and −1.5 V, the intercalation of ions causes the kinetic polarization of the electrode and rather high residual currents in the potential range between 0.4 V and −0.4 V. However, if the electrode is polarized in a restricted potential range between 0.2 V and −0.2 V, in which there are no faradaic reactions of Co(II)Pc microcrystals and consequently no inclusion of K^+ or NO_3^- ions, the response consists solely of a capacitive current which is about hundred times smaller than the residual current shown in Fig. 1. Under these conditions the response of sulfide oxidation can be observed. Similar effects of counterions have been obtained with polymer films [34].

Figure 2 shows cyclic voltammograms of electrooxidation of $10^{-3}M$ Na_2S which is catalysed by Co(II)Pc microcrystals immobilized at the surface of PIGE in 1 *M* KNO_3 at pH 9.22. In the absence of Na_2S, Co(II)Pc immobilized at PIGE is not electroactive between −0.2 and 0.3 V (broken line in Fig. 2). Also, at a clean PIGE, without Co(II)Pc, no response of Na_2S oxidation was observed in this potential range. Catalytic electrooxidation of HS^- proceeds in two steps. Its CV consists of two oxidative peaks, at −0.120 and 0.17 V, and a reductive peak at −0.122 V, which are marked I, II and III, respectively. If the cycling is restricted to the potential range between −0.3 and 0.05 V, only peaks I and III appear, both at the potential of −0.122 V, and their peak currents are similar: $i_{P,I} = 0.31\ \mu A$ and $i_{P,III} = 0.25\ \mu A$. Peak

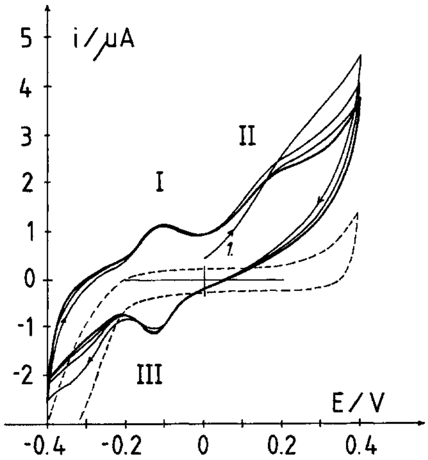

Fig. 2. Cyclic voltammograms of $10^{-3}M$ Na_2S on Co(II)Pc/PIGE in 1 M KNO_3, pH 9.22. $E_{st} = 0$ V, $v = 100$ mV/s, the first scan is marked. Broken line: the response of Co(II)Pc/PIGE in the absence of Na_2S

current II is proportional to the concentration of Na_2S, and increases if the solution is stirred.

Dependences of the oxidation peak currents I and II and the reduction peak current III on the concentration of Na_2S are shown in Figs. 3a and 3b, respectively. Below 10^{-5} M Na_2S, peak current I is too small to be measured, and below 10^{-6} M Na_2S peak III also disappears. The oxidation peak current II depends linearly on Na_2S concentration in the range from 10^{-4} to 10^{-3} M. This peak is not measurable below 10^{-4} M Na_2S. Dependences of the peak currents I and III on Na_2S concentration suggest the saturation of the electrode surface. In 10^{-3} M Na_2S the peak currents I and II are linearly proportional to the square-root of the scan rate, which indicates that their reactants are dissolved species. Peak current III is a linear function of scan rate between 20 mV/s and 5 V/s, which is typical for a surface-confined reactant. This would mean that the product of the first electrooxidation of HS^- remains bound to the electrode surface. In $10^{-3}M$ Na_2S the relationship between peak potentials of III and the logarithm of the scan rate shows the change from reversible to totally irreversible reaction. The slope $\Delta E_P(\mathrm{III})/\Delta\log(v) = -63$ mV, which appears for $v > 1$ V/s, indicates that most probably $n = 2$ and $\alpha = 0.45$. Similar values are calculated from half-peak widths of III: $n = 2$ and $\alpha = 0.4$.

Dependences of peak potentials of the first oxidation $E_P(\mathrm{I})$ and the reduction $E_P(\mathrm{III})$ processes on the logarithm of Na_2S concentration are shown in Fig. 4. The relationship between $E_P(\mathrm{I})$ and $\log[Na_2S]$ is linear, with a slope of -59 mV. This is characteristic of totally irreversible oxidation which is second order in HS^-. This relationship is demonstrated in the Appendix. The slope corresponds to the product $\beta n = 1$, where β is a transfer coefficient of the oxidation process and n is the number of electrons in the oxidation. The reduction peak potentials are influenced only in the range of higher Na_2S concentrations, with the slope $\Delta E_P(\mathrm{III})/\Delta\log([Na_2S]) = -30$ mV.

These results can be explained by the mechanism which was proposed by Allen and Hickling [35]. The

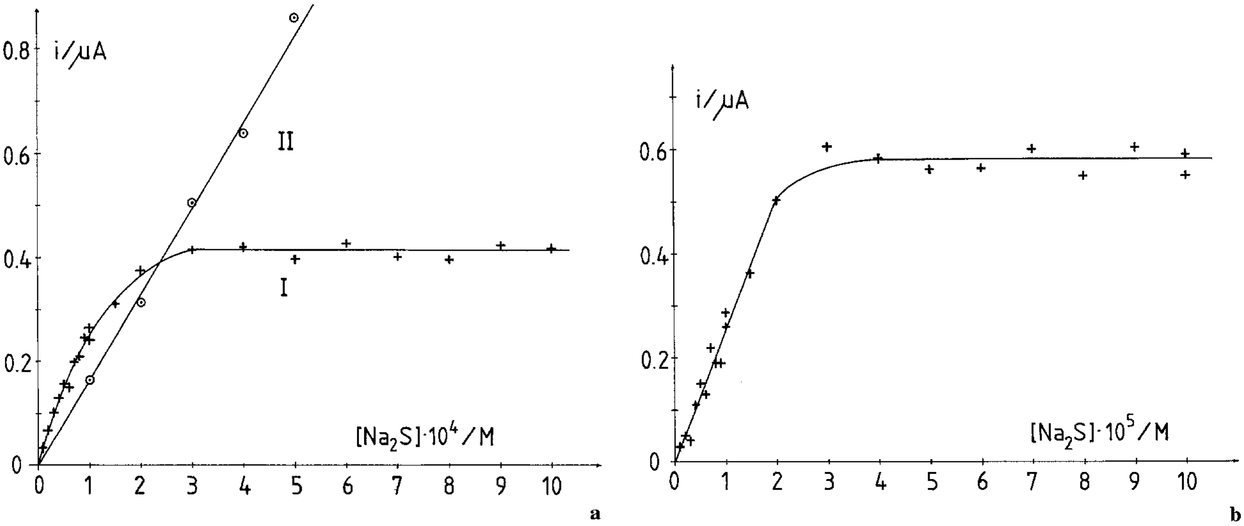

Fig. 3. Dependence of **a** the first (I) and second (II) oxidation peak currents and **b** the reduction peak currents (III) on Na_2S concentration. Conditions: $v = 100$ mV/s, $E_{st} = -0.25$ V, Co(II)Pc/PIGE, pH 9.22, 0.5 M KNO_3

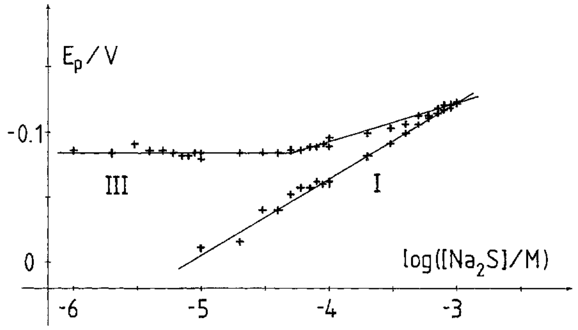

Fig. 4. Dependence of CV peak potentials of the first oxidation (*I*) and the reduction (*III*) processes on the logarithm of Na_2S concentration. Conditions as for Fig. 3

first oxidation step is irreversible and second order in HS^-. Its products is the adsorbed disulfide:

$$2HS^- + OH^- + K^+ \rightarrow (KHS_2)_{ads} + 2e^- + H_2O \quad (1)$$

The second oxidation peak develops at more positive potentials. It is catalysed by the adsorbed species:

$$2HS^- + OH^- \rightarrow HS_2^- + 2e^- + H_2O \quad (2)$$

If the concentration of dissolved sulfide ions is lower than $10^{-4} M$, the adsorbed disulfide dissociates and leaves the adsorbed sulfur atoms at the electrode surface:

$$(KHS_2)_{ads} \leftrightarrow S_{ads} + HS^- + K^+ \quad (3)$$

Peak III corresponds to the reduction of the adsorbed sulfur:

$$S_{ads} + 2e^- + H_2O \rightarrow HS^- + OH^- \quad (4)$$

This simplified mechanism explains the main experimental results. It is similar to the mechanism of HS^- oxidation at a gold electrode [6]. It was shown that isolated molecules such as AuS [6] and CuS [8] deposited on the surface of an inert electrode exhibit high electrocatalytic activity towards oxidation of sulfide ions. Hence, the adsorbed sulfur may serve as a bridge for the charge transfers. This adsorption is probably the formation of an adduct to cobalt phthalocyanine, but we have not enough evidence to prove it. The supposed adduct facilitates the oxidation of the dissolved HS^- ions. It is proposed that the initial charge transfer includes the reduction of the metal ion in the phthalocyanine [14]. The charge is then transferred to carbon particles by electrons hopping between the neighbouring metal centers because Co(I) is not stable at these electrode potentials. These intermediate steps may influence the overall rate of the redox reaction [4, 33, 36]. These results show that solid compounds such as Co(II)Pc microcrystals can catalyse both the electrooxidation of HS^- ions and the electroreduction of surface-bound sulfur atoms. They are in agreement with the reports of Tse et al. [14, 15] and demonstrate that abrasive stripping voltammetry can be used for the initial investigation of the assumed catalytic properties of various solid compounds.

Appendix

A theory of reversible, second order redox reaction:

$$2R \rightleftharpoons O_2 + ne^- \quad (I)$$

has been developed for cyclic voltammetry [37], and here the solution for irreversible reaction (I) under steady-state conditions is presented. The steady fluxes and the current are defined as:

$$(\partial c_R/\partial x)_{x=o} = [c_R^* - (c_R)_{x=o}]/\delta = -i/nFSD \quad (A1)$$

$$(\partial c_{O_2}/\partial x)_{x=o} = -(c_{O_2})_{x=o}/\delta = i/2nFSD \quad (A2)$$

$$i/nFS = -k_s \exp(\beta\psi)(c_R)_{x=o}^2 \quad (A3)$$

where: $\psi = (nF/RT)(E - E_f^o)$, $E_f^o = E^o - 2.3\,(RT/\,nF)\,\mathrm{pH}$, c_R^* is the bulk concentration of the reduced species R, $(c_R)_{x=o}$ and $(c_{O_2})_{x=o}$ are the concentrations of the reduced and the oxidized species R and O_2 at the electrode surface, δ the diffusion layer thickness, i the current, n the number of electrons, F the Faraday constant, S the electrode surface area, D the common diffusion coefficient, k_s the standard reaction rate constant, β the transfer coefficient for the oxidation and E^o the standard potential.

The solution of Eqs. (A1)–(A3) is:

$$\phi_{ss} = [-(2u+1) + (4u+1)^{1/2}]/2u \quad (A4)$$

where: $\phi_{ss} = i\delta(nFSDc_R^*)^{-1}$ is a dimensionless current, $u = \kappa^* \exp(\beta\psi^*)$, $\kappa^* = k_s\delta(c_R^*)^\alpha/D$, $\alpha = 1 - \beta$, $\exp(\psi^*) = c_R^* \exp(\psi)$, $\psi^* = (nF/RT)(E - E_f^*)$ and $E_f^* = E_f^o - (RT/nF)\ln(c_R^*)$.

The dimensionless current changes from $\lim_{\psi \to -\infty}(\phi_{ss}) = 0$ to $\lim_{\psi \to \infty}(\phi_{ss}) = -1$.

This is the polarographic wave, and its half-wave potential is defined by the conditions $u_{1/2} = 2$, wherefrom:

$$E_{1/2} = E_f^o + (RT/\beta nF)\ln(2D/k_s\delta) - (RT/\beta nF)\ln(c_R^*) \quad (A5)$$

$$\partial E_{1/2}/\partial \log(c_R^*) = 2.3(RT/\beta nF) \quad (A6)$$

The basic thermodynamic relationship (A6) applies also to the peak potential in the cyclic voltammetry, which we proved by numerical simulation.

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