Full Paper

Electrocatalytic Oxidation of Dithionite at a Cobalt(II)tetrasulfonated Phthalocyanine and 5,10,15,20-Tetrakis-(4-sulfonatophenyl)porphyrin Cobalt(II) Modified Gold Electrode in Alkaline Solution

Karolien De Wael,[a] *Philippe Westbroek,*[*b] *Eduard Temmerman*[a]

[a] Ghent University, Department of Analytical Chemistry, Krijgslaan 281 S12, B-9000 Gent, Belgium
[b] Ghent University, Department of Textiles, Technologiepark 907, B-9052 Gent, Belgium
*e-mail: philippe.westbroek@Ugent.be

Abstract

In this paper it is shown that the charge transfer kinetics of the oxidation of sodium dithionite at a gold electrode in alkaline solution can be increased by modifying this electrode with cobalt(II)tetrasulfonated phthalocyanine, sodium salt (CoTSPc) or 5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin cobalt(II), tetrasodium salt (CoTSPor). Electrodeposition of these catalysts is discussed as well as the oxidation of sodium dithionite at these immobilized catalysts. Despite an observed acceleration in the charge transfer kinetics, sodium dithionite is still oxidized irreversibly. However, the improvement in kinetics has beneficial consequences in the field of electroanalysis of sodium dithionite. Comparison of the oxidation at bare gold and modified gold electrodes showed that with improved charge transfer kinetics at the modified electrodes a higher sensitivity and selectivity and a much lower detection limit is obtained.

Keywords: Gold, Electrocatalysis, Sodium Dithionite, Oxidation

1. Introduction

Sodium dithionite finds several applications as a reducing agent, such as in the reduction of textile dyes for dyeing processes. This reduction is crucial for the process because the oxidized form of most of these dyes (indigo, indanthrenes, …) is virtually insoluble in aqueous solutions. However, sodium dithionite is relatively unstable and reacts with oxygen, which may cause a fast decline of its concentration during processing [1–2]. This can have a serious influence on the actual reduced dye concentration and on the quality and reproducibility of the dyed textile product.

In the past, Westbroek et al. devoted research to the development of sensors to measure concentrations of chemical components important in the textile industry, such as hydrogen peroxide in bleaching [3–6], sodium dithionite [7–10] and sulfite [8, 10] in dyeing as well as the dyes themselves such as indigo [10] and indanthrenes [7, 9]. They focussed mainly on voltammetric and amperometric detection of these components using rotating disc [3–9], ultramicro [5] and wall-jet electrodes positioned in flow through cells [10]. To support the insight in the analytical determination of the concentration of the above mentioned chemicals they also investigated the mechanism [11–13], kinetics [11–14] and reagent transport properties [8, 1–14] of the oxidation/reduction reactions used for their analytical detection.

The reason to start the above mentioned investigations on sodium dithionite and associated dye sensor development was the fact that drawbacks of previously developed methods prevented their widespread use in practice. Several methods were described in literature to determine the concentration of sodium dithionite, sulfite [15–20] and/or indigo [20–22]. The sodium dithionite concentration can be determined by volumetric titration with jodium [15–17] or with $K_3[Fe(CN)_6]$ [20]. The endpoint detection of these titrations can be done visually [17–19] or potentiometrically [18–19]. Besides a fotometric and spectrofotometric reflectance method [21–22], indigo can be determined by potentiometric titration [20]. The difference in standard potential of indigo and sodium dithionite is about 150 mV, which allows determination of both concentrations in the same titration [20].

In this paper the authors will show that the detection of sodium dithionite on bare gold electrodes can be improved by electrocatalysis using a cobalt(II)tetrasulfonatedphthalocyanine, sodium salt (CoTSPc) (Fig. 1a) or a 5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin cobalt(II), tetrasodium salt (Fig. 1b) (CoTSPor) as catalyst.

The choice for these catalysts was based on their well described behavior in literature (but not in combination with gold), the knowledge in electrodeposition of these compounds on gold surfaces and their good water solubility, making it possible to perform electrodeposition in aqueous (read environmental friendly) solutions.

a)

b)

Fig. 1.   Molecular structure of cobalt(II)tetrasulfonatedphthalocyanine, sodium salt (a) and 5,10,15,20-tetrakis-(4-sulfonatophenyl)por-phyrin cobalt(II), tetrasodium salt (b).

2. Experimental

A saturated calomel reference electrode (SCE) with two compartments from Radiometer and a carbon counter electrode were used. The working electrodes were gold electrodes from BAS (diameter 1.6 mm) and were pre-treated by mechanical and electrochemical polishing. Be-fore 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 is further subjected to sequential polishing on polishing cloth covered with alumina (Buehler) powder of 1, 0.3 and 0.05 μm particle size for respectively 5, 10 and 20 minutes. To remove any adherent Al_2O_3 particles the electrode surface was rinsed

thoroughly with doubly deionized water and cleaned in an ultrasonic bath (Branson 3210) for 2 minutes. Finally the electrode was pretreated electrochemically by scanning it in a buffer solution, pH 12, between − 1.2 and 0.6 V (vs. SCE) until 5 subsequent scans were identical.

A PGSTAT20 potentiostat from ECO Chemie 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 CoTSPc sodium salt was purchased from Midcentury (Posen, Il, USA). The buffer solution of pH 12 (Na_2HPO_4/NaOH) and sodium dithionite were purchased from Riedel-de Haën. CoTSPor tetrasodium salt was obtained from Porphyrin
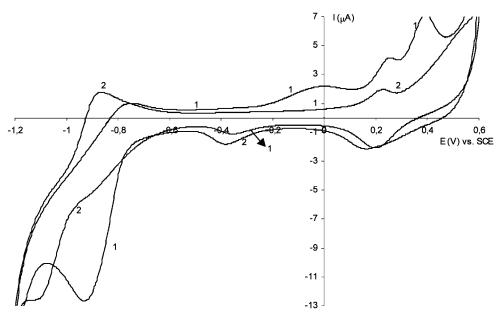
Fig. 2. Current-potential curves recorded at CoTSPc (curve 1) and CoTSpor (curve 2) modified gold electrodes in pH 12 buffer solution containing 8×10^{-3} mol L^{-1} CoTSPc (curve 1) or CoTSpor (curve 2).

Systems (Lübeck, Germany). Before each experiment, pure nitrogen was bubbled through the cell solution for 20 minutes.

3. Results and Discussion

3.1. Electrodeposition of the Catalysts

Prior to each deposition experiment a tenfold scanning of the gold electrode was performed between -1.2 and 0.6 V (vs. SCE) in a pH 12 buffer solution. The deposition itself consists of scanning the electrode for about 100 scans in the same potential window in a pH 12 buffer solution containing 8×10^{-3} mol L^{-1} of CoTSPc or CoTSPor. Figure 2 shows the final scans of the deposition of CoTSPc (curve 1) and CoTSPor (curve 2).

It can clearly be seen that for both catalysts, peaks due to metal ion oxidation/reduction occur at potentials around -0.3 and 0.2 V (vs. SCE) and around -0.9 and -1.1 V (vs. SCE) for ring activity. Additionally for CoTSPc also an oxidation peak is detected around 0.4 V (vs. SCE) (curve 1). The intensity of these peaks increased gradually with scanning of the electrode in the buffer containing CoTSPc or CoTSP until a stable curve was obtained, curves 1 and 2 in Figure 2.

The reversibly behaving redox system around 0.2 V (vs. SCE) can be attributed to Co(III)/Co(II) [23–26] and Co(II)/Co(I) [26–28] corresponds to the quasi reversible system around -0.3 V (vs. SCE). Reduction peaks around -0.9 and -1.1 V (vs. SCE) correspond to ring reduction of Co(II)TSPc at Co(II)TSPc modified gold surfaces as confirmed by literature results [26].

A hypothesis for the electrodeposition of Co(II)TSPc at gold electrode surfaces has been formulated [26] based on electrochemical observations by correlating the evolution in

time of the different peaks observed as a function of scan number and Co(II)TSPc concentration in solution. Peaks due to Co(III)/Co(II) and Co(II)/Co(I) redox systems were indentified and ring oxidation/reduction peaks were observed. In addition, some of these peaks showed electrocatalytic activity for respectively reduction or oxidation of Co(II)TSPc at the Co(II)TSPc modified gold electrode. The mechanism of deposition was found to be a multistep process where running through the entire anodic and cathodic potential window is an important condition, initial deposition is controlled by kinetics and reorganization of the initially formed layer occurs as a function of time. Only when the procedure given above final voltammetric curves are obtained as shown in Figure 2. These curves are suitable for further work according to the electrocatalytic oxidation of sodium dithionite.

3.2. Electrocatalysis with Modified Gold Electrodes Towards Sodium Dithionite

Common possible steps in an overall electrochemical reaction are electron transfer, chemical reaction, transport and ad(de)sorption steps, the slowest one being rate determining.

It is known that depositing a catalyst at the surface of an electrode can increase the reaction rate, in general by accerelerating the charge transfer or chemical reaction kinetics. This means that if improvement of the overall electrochemical reaction rate is the goal, such a kinetic step should be rate determining at the unmodified electrode. This also means that for redox systems behaving reversibly at the unmodified electrode, electrocatalysis is not useful because for reversible systems transport controls the overall rate of the reaction at all potentials.
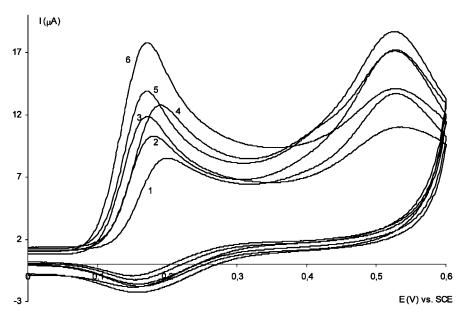
Fig. 3. Voltammetric curves of sodium dithionite at a bare gold electrode (curves 1 and 4), at a CoTSPc modified gold electrode (curves 2 and 5) and at a CoTSPor modified gold electrode (curves 3 and 6), in pH 12 buffer solution containing 9.85×10^{-4} (curves 1, 2 and 3) and 1.46×10^{-3} mol L^{-1} (curves 4, 5 and 6) of sodium dithionite. $T = 298.0$ K; $v = 50$ mV s^{-1}.
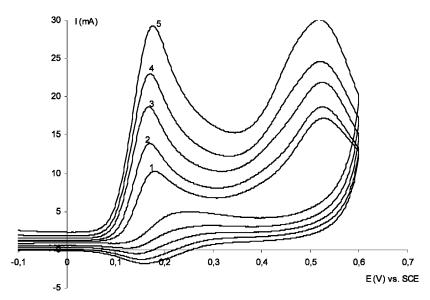

Fig. 4. Oxidation of sodium dithionite at a CoTSPc modified gold electrode in a pH 12 buffer solution containing 1) 9.85×10^{-4}, 2) 1.46×10^{-3}, 3) 1.93×10^{-3}, 4) 2.39×10^{-3} and 5) 2.84×10^{-3} mol L^{-1} of sodium dithionite. $T = 298.0$ K; $v = 50$ mV s^{-1}.

Despite the fact that for the oxidation of sodium dithionite at unmodified gold electrodes well-defined voltammetric waves are obtained [12], the reaction still behaves irreversibly [12–14]. Therefore it is in principle possible to improve the oxidation rate of this reaction by using an appropriate catalyst immobilized at the gold electrode surface.

In Figure 3 cyclic voltammetric curves are shown of the oxidation of sodium dithionite at a gold electrode (curves 1, 4), at a CoTSPc modified gold electrode (curves 2, 5) and at a CoTSPor modified gold electrode (curves 3, 6) for two different sodium dithionite concentrations. Several obser-

vations indicate electrocatalytic behavior. First the voltammetric waves are shifted towards less positive potentials. This means that less overpotential (or generally activation energy) should be applied to the system because of the presence of CoTSPc that provides an alternative, less energy demanding, oxidation reaction path for sodium dithionite. Secondly, the slope of the inclining part of the wave is higher at the modified electrodes, revealing faster charge transfer kinetics. Thirdly, the shape of the voltammetric wave is better defined (more peak shaped wave) and the peak currents are higher compared to the peak currents obtained at an unmodified electrode. Finally, experiments with
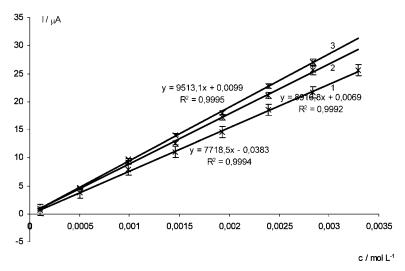
Fig. 5. Calibration plot between peak current of the sodium dithionite oxidation reaction and its concentration at a bare gold electrode (plot 1) and at a CoTSPc (plot 2) and CoTSPor (curve 3) modified gold electrode. $T = 298.0$ K.

varying concentrations of sodium dithionite at gold electrodes and CoTSPc modified gold electrodes (Fig. 4) showed that the peak current shift towards more positive potentials is much more expressed at unmodified gold electrodes than is the case at the modified ones. This again indicates that for the modified electrodes the influence of the charge transfer kinetics in the overall oxidation rate is smaller. Important to note is that the oxidation of sodium dithionite at the modified gold electrodes is still behaving irreversibly, so charge transfer kinetics still play a role in the overall rate, especially at small overpotentials.

Another remark is the relatively mild electrocatalytic effect resulting in a shift of the wave of 20 mV and an increase of the peak currents by approximately 17%. This can be explained by the fact that the dithionite oxidation at bare gold occurs with relatively fast kinetics (well-defined, transport controlled peak), despite the irreversible behavior of this reaction. Therefore, it may be clear that it is not possible to improve much on the kinetics. This partly explains the relatively mild electrocatalytic effect of CoTSPc. Another reason is that the oxidation of dithionite is performed at Co(III)TSPc, a species that first needs to be formed at the electrode surface. From Figure 2 it can be seen that its formation is complete around 0.1 V (vs. Ag | AgCl), the same potential where the oxidation of dithionite at CoTSPc starts to occur.

Electrocatalysing the oxidation of sodium dithionite has advantageous consequences for its analytical application, especially in sensor development to monitor the sodium dithionite concentration during processing. Calibration plots obtained at gold electrodes and CoTSPc modified gold electrodes (Fig. 4) are shown in Figure 5. The peak currents of these calibration plots are the net peak currents, obtained by subtracting the background current recorded at $E = 0$ V (vs. SCE) from the experimental peak current. Note that this background current is dependent on the dithionite concentration (see Fig. 4) for both modified and unmodified electrodes. However, repetition of the concentration studies

showed that this current is very reproducible for the modified electrodes, which is not the case for the unmodified ones. This explains why the error margins (Fig. 5) for unmodified electrodes were relatively high, especially for small concentrations.

The large difference in error margin observed at the bare gold and modified gold electrode also has its consequences on the detection limit. Taking into account the criterion that the detection limit corresponds to twice the standard deviation results in a detection limit of about 2×10^{-4} mol L^{-1} for the unmodified gold electrode, which was also found in literature [10], and 8×10^{-6} mol L^{-1} for the modified electrode. As mentioned above, this is mainly due to a much more stable and reproducible background current.

From Figure 5 it can also be seen that the sensitivity of the detection of sodium dithionite has improved on the modified gold electrode because a higher slope is obtained for the calibration plot.

Finally it can be observed from the curves in Figure 3 that the second oxidation peak of dithionite (due to oxidation of sulfite to sulfate [7, 8, 10, 12, 13]) does not shift to less positive potentials at modified gold electrodes. In other words this reaction is not electrocatalyzed. This means that a better peak separation will be obtained at the modified electrode or a higher selectivity for dithionite will be obtained.

4. Conclusions

It is clearly shown in this paper that CoTSPc or CoTSPor modified gold electrodes electrocatalyze the charge transfer kinetics of the oxidation of sodium dithionite. This is beneficial for the analytical detection of sodium dithionite because it improves sensitivity, selectivity and detection limit. This is important for industrial applications because a more precise and accurate monitoring of sodium dithionite concentration during processing will lead to a more efficient

use of the chemicals. This makes it possible that less chemical will be consumed and that waste water from the process is less heavily loaded with hazardous compounds.

5. References

[1] F. Camacho, P. Paez, C. Jimenez, M. Fernandez, *Chem. Eng. Sci.* **1997**, *52*, 1387.

[2] A. A. Shaikh, S. M. Zaidi, *J. Chem. Technol. Biotechnol.* **1993**, *56*, 139.

[3] P. Westbroek, E. Temmerman, P. Kiekens, *Anal. Commun.* **1998**, *35*, 21.

[4] P. Westbroek, E. Temmerman, P. Kiekens, *Anal. Chim. Acta* **1999**, *385*, 423.

[5] P. Westbroek, B. Van Haute, E. Temmerman, *Fres. J. Anal. Chem.* **1996**, *354*, 405.

[6] P. Westbroek, E. Temmerman, P. Kiekens, F. Govaert, *J. Autom. Chem.* **1998**, *20*, 185.

[7] F. Govaert, E. Temmerman, P. Westbroek, *Anal. Commun.* **1998**, *35*, 153.

[8] E. Gasana, P. Westbroek, E. Temmerman, H. P. Thun, *Anal. Commun.* **1999**, *36*, 387.

[9] F. Govaert, E. Temmerman, P. Kiekens, *Anal. Chim. Acta* **1999**, *385*, 307.

[10] E. Gasana, P. Westbroek, E. Temmerman, H. P. Thun, P. Kiekens, *Anal. Chim. Acta* **2003**, *486*, 73.

[11] P. Westbroek, E. Temmerman, *J. Electroanal. Chem.* **2000**, *482*, 40.

[12] P. Westbroek, J. De Strycker, K. Van Uytfanghe, E. Temmerman, *J. Electroanal. Chem.* **2001**, *516*, 83.

[13] E. Gasana, P. Westbroek, K. De Wael, E. Temmerman, K. De Clerck, P. Kiekens, *J. Electroanal. Chem.* **2003**, *553C*, 35.

[14] E. Gasana, P. Westbroek, E. Temmerman, H. P. Thun, F. Twagiramungu, Electrochem. Commun. **2000**, *2*, 727.

[15] L. Brown, L. Szekeres, *Talanta* **1979**, *26*, 414.

[16] W. P. Kilroy, Talanta **1979**, *27*, 343.

[17] W. P. Kilroy, Talanta **1983**, *30*, 419.

[18] E. P. Serjeant, *Potentiometry and Potentiometric Titrations*, Wiley, Chichester **1984.**

[19] A. J. Bard, R. Parsons, J. Jordan, *Standard Potentials in Aqueous Solution*, Marcel Dekker, New York **1985.**

[20] U. Baumgartner, *Mell. Textilber.* **1987**, *68*, 189.

[21] R. C. Denney, R. Sinclair, *Visible and Ultraviolet Spectroscopy*, Wiley, Chichester **1987.**

[22] T. Bechtold, E. Butscher, O. Bobleter, *Textil Praxis Int.* **1992**, *6*, 44.

[23] K. Ozoemena, P. Westbroek, T. Nyokong, *J. Porphyr. Phthalocyanine* **2002**, *6*, 98.

[24] A. B. Lever, A. Milaeva, G. Speier, in *Phthalocyanines: Properties and Applications* (Eds: C. C. Leznoff, A. B. Lever), VCH, New York **1989.**

[25] A. R. Ozkaya, E. Hamuryudan, Z. A. Bayir, O. Bekaroglu, *J. Porph. Phthal.* **2000**, *4*, 689.

[26] K. De Wael, P. Westbroek, E. Temmerman, *J. Electroanal. Chem.*, in press.

[27] C. C. Leznoff and A. B. P. Lever, *Phthalocyanines: Properties and Applications*, Vol. 3, VCH, Weinheim **1993.**

[28] K. Ozoemena, P. Westbroek, T. Nyokong, *Electrochem. Commun.* **2001**, *3*, 529.

[29] J. Zagal, R. K. Sen and E. Yeager, *J. Electroanal. Chem.* **1977**, *83*, 207.