Electrochemistry of a carotenoid self-assembled monolayer

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Abstract

A carotenoid self-assembled monolayer was prepared by dipping a gold electrode into a solution of 4'-thioxo-*β,β*-caroten-4-one in acetonitrile. Electrochemistry of the surface layer was investigated by cyclic voltammetry in an aqueous solution. No electrochemical reaction was detected in the potential region between 0.5 and -0.6 V *vs*. SCE. The anodic reaction of adsorbed carotenoid occurs at 0.8, whereas the irreversible anodic desorption proceeds at 1.4 V in 0.01 M $HClO_4$. Formation of the surface layer resulted in a decrease of the charging current as well as in a strong inhibition of the electron transfer reaction for species such as $Fe(CN)_6^{3-}$, $Ru(NH_3)_6^{3+}$, and dissolved oxygen. Prolonged voltage cycling in the O_2 reduction range induced some changes in the surface layer characteristics that were tentatively accounted for by the cross-linking of adsorbed molecules under the effect of transient oxygen radicals.

Keywords: Self-assembled monolayers; Carotenoids; Thiones; Voltammetry; Gold electrode; Chemisorption

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1. Introduction

Although an abundant literature on self-assembled monolayers (SAMs) of saturated thiols on metal surfaces is available [1-4], SAMs of unsaturated sulfur derivatives have been less investigated. Research in this field was mostly oriented to thioaromatic compounds, with a particular stress on prospective applications in the field of molecular scale electronics [5, 6].

Owing to their availability, carotenoids could be a suitable alternative for building-up molecular wires. In this respect, the ohmic behaviour of an isolated carotenoid molecule, as evidenced by Leatherman et al. [7], is a promising feature.

Two problems arise when attempting to set-up a contact between a metal and a molecule-conductor: the anchoring procedure and the stability of the organic compound at the metal surface. Based on these considerations, we attempted to prepare and assess a SAM formed by chemisorption of 4'-thioxo-*β,β*-caroten-4-one (**I,** Scheme 1) on a gold electrode. This communication reports preliminary results on formation, stability and compactness of such a layer in contact with an aqueous solution. Linear scan cyclic voltammetry (CV) was used as experimental method.

To our knowledge, this is the first report on electrochemistry of carotenoids in the SAM form. So far, investigation in electrochemistry of carotenoids has been performed in non-aqueous media [8 - 10] with the notable exception of some studies in micelle systems [11]. The SAM form would allow investigating carotenoids in direct contact with an aqueous phase. Such conditions are closer to the natural carotenoid surrounding in the living cell and offer the opportunity to ascertain the effect of factors such as pH or ion content of the solution. It is clear that a mixed SAM monolayer of carotenoid/alkane thiol might achieve this biomimicity better. However, the investigation of the plain carotenoid layer is a compulsory step before approaching a more intricate composition.

2. Experimental

4'-thioxo-*β,β*-caroten-4-one (**I**) was synthesised and characterised as described previously [12]. A fresh, $5\cdot10^{-5}$ M solution in oxygen-free acetonitrile was prepared daily and stored under nitrogen atmosphere.

A gold disk electrode was prepared by embedding a gold wire (Aldrich, 99.99%, 0.5 mm diameter) in a glass tube with Epoxy resin. Electrode surface was prepared by mechanical polishing followed by continuous cycling in 10^{-2} M $HClO_4$ (potential range from 0.00 to 1.45 V; scan speed, 20 mV/s) until the CV record showed the characteristic pattern of the pure surface [13].

The electrochemical cell was fitted with an Ag|AgCl|KCl(1M) reference electrode (connected via a 1 M KNO_3 bridge) and a Pt wire as auxiliary electrode. Reported potential electrodes refer to the saturated calomel electrode (SCE). Voltammetric experiments were run at $20 \pm 1°$ C by means of conventional equipment. Dissolved oxygen was expelled from the test solution by a stream of pure nitrogen prior to the CV run. An air saturated 0.01 M $HClO_4$ solution was used in oxygen reduction experiments.

The SAM was prepared *ex situ* by dipping the gold electrode for 10 to 60 min. into a fresh, $5 \cdot 10^{-5}$ M compound (**I**) solution in acetonitrile, under continuous nitrogen purging. The electrode was then rinsed with pure acetonitrile and de-ionised water and then transferred to an aqueous solution for voltammetric investigation.

3. Results and discussion

(i) Anodic voltammetry in acid solution

Due to the presence of the sulfur function, the compound (**I**) is expected to adsorb at the gold surface by means of a sulfur anchor. Electrochemical reactivity of the surface layer is illustrated by Fig. 1, which displays three distinct potential regions: (i) the double layer region (from 0.6 to 0.8 V), (ii) the anodic reaction of adsorbed carotenoid (peak A), and (iii) anodic desorption of the surface layer accompanied by gold oxidation (peak B). Gold oxide reduction during the reverse scan occurs in the region of peak C. These assignations are further substantiated by experimental results.

The charging current recorded in the double layer region (under saturation conditions) decreases as a consequence of compound (**I**) adsorption, but the variation is not as high as noticed with a long-chain alkane thiol [2]. This difference could be due to the higher polarizability of the carotenoid molecule, leading to a higher dielectric constant as compared to that of an alkane thiol.

The shoulder A lays in the characteristic potential region of the anodic process in a non-aqueous solution of some oxygen substituted carotenoids [8]. The anomalous shape of the peak A is due to the interference with peak B. However, a background subtracted voltammogram displays A as a symmetrical peak, as typical for a surface confined charge transfer reaction. If the anodic limit in the CV run is set at 1.0 V vs. SCE (to avoid the anodic desorption, Inset to Fig. 1), the irreversible character of the peak A process is evident. It may be inferred that the primary product of the electron transfer reaction (probably a cation-radical, by analogy with the results in ref. [8]), reacts rapidly with the aqueous environment to give an inactive product. Such a fast decay has already been noticed for electrochemically generated carotene radicals in micelle systems [11].

In conclusion, it is the product of the anodic oxidation (peak A), and not the initially adsorbed form, which is involved in the anodic desorption process. It is likely that the product of the peak A reaction preserves a high degree of non-saturation.

SAM stability in the anodic region was assessed by multiple CV scans in 0.01 M $HClO_4$ (Fig. 1). The first anodic scan (curve 1) displays the peak B, which is analogous to that evidenced for a SAM formed by a short-chain thioalkane [2]. Consequently, this peak is assigned to the anodic desorption of the surface layer caused by the oxidation of sulfur function. Simultaneously, gold is oxidised, as demonstrated by the occurrence of peak C arising from gold oxide reduction. Subsequent scans (Fig. 1, curves 2 to 4) result in CV patterns which are alike to those recorded at a plain gold electrode (Fig. 1, curve 5), proving the irreversible character of the desorption process. Peak B current increases with increasing the adsorption time (t) and tends to level off at $t > 60$ min. The same trend was noticed for peak A.

The Q_{des}/Q_A ratio (where Q_{des} stands for the electrical charge associated with the anodic desorption and Q_A is the peak A charge) varies randomly between 3 and 4 when the modification time varies between 30 s and 30 min. The main source of incertitude lays in the extremely low values of peak A current. A Q_{des} / Q_A ratio of 3 may be accounted for by assuming that the process A involves a single electron transfer, whereas the anodic desorption implies 3 electrons, as in the case of thioalkanes [2]. Further investigations by means of the electrochemical quartz crystal microbalance are required in order to determine the surface coverage and elucidate the stoichiometry of the anodic reactions.

A pH increase from about 2 (Fig. 1) to 7 (phosphate buffer) shifts the peak B potential from 1.4 V to 1.1 V. Under the same conditions, the gold anodic process (at a naked electrode) suffers an even larger shift (up to about 0.8 V). Such a different behaviour suggests that the pH dependence of the peak B potential is not a consequence of an easier gold oxidation. It could rather be inferred that proton release during the oxidative desorption is the reason for the pH effect on peak B. This effect could be associated to oxygen transfer to the sulfur function during the anodic desorption process, probably by a mechanism alike to that represented by equation (3) in ref. [2].

(ii) Cathodic voltammetry in the absence of dioxygen

In order to investigate the cathodic behaviour of the carotenoid covered electrode, the potential was scanned between 0.0 and -1.4 V in 0.1 M KOH. The state of the surface was subsequently assessed by performing an anodic scan in 0.01 M $HClO_4$, as in Fig. 1. No cathodic desorption peak was noticed on the CV record. After a single CV cathodic scan experiment, the subsequent anodic scan reveals only slight modifications in the behaviour of the surface layer. However, prolonged repetitive scans in the cathodic region induce the gradual desorption of the surface layer. In contrast, cathodic desorption of alkane thiols gives rise to a characteristic peak and desorption is completed after a few scans [2].

In conclusion, when compared with a SAM of a long chain alkane thiol [2], the SAM prepared from the thione (**I**) is more stable in the cathodic region, but less stable in the anodic one. This difference could be rationalised with the sulfur site in a carotenoid derivative having higher electron density, caused by the extended double bond conjugation. Such a charge distribution facilitates the electron release in the anodic desorption but makes the electron uptake in the cathodic process to be more difficult.

(iii) Charge transfer reactions at the modified electrode

The packing degree of the carotenoid adsorbed layer was assessed by its blocking effect on the electrochemical reactions of $Fe(CN)_6^{3-}$ (Fig. 2a) and $Ru(NH_3)^{3+}$ (Fig. 2b) In this experiment, the electrode potential was confined to the double layer region, where the adsorbate is not electrochemically active. As a consequence of the partial surface blocking, the ferricyanide voltammogram shows the typical pattern for an array of independent ultramicroelectrodes. However, a treatment of the CV data by means of the pinhole model [2] leads to some differences between the parameters of the pinhole array as obtained by means of different redox probes (Table 1). Probably, ferricyanide partition between the surface layer and the solution (as described in ref. [17]) plays a role in the system under investigation.

The above results prove that the adsorption of thione (**I**) on a polycrystalline gold surface yields an adsorbed layer with a high degree of compactness, although not completely impermeable to ions in solution.

(iv) Cathodic voltammetry in the presence of dioxygen

Carotenoids react with free radicals, including oxygen radical species [18]. Therefore, the adsorbed layer was exposed to the products of oxygen reduction. Oxygen reduction to H_2O_2 gives rise to transient radicals, such as $O_2\cdot^-$ or HOO· [19] that are expected to interact with the non-saturated adsorbate inducing specific changes in the properties of the adsorbed layer. As a first effect, it was found that O_2 reduction on the carotenoid covered surface is shifted by 0.2 V in the negative direction relative to the plain electrode (Fig. 3a, curves 1 and 2). It was further noticed that repetitive CV scans in the O_2 reduction region (+0.10 to -0.55 V vs. SCE) at the carotenoid covered electrode causes the O_2 wave to shift to more negative potentials until it coalesces with the hydrogen evolution current and cannot be distinguished any longer (Fig. 3a, curves 2 – 5*)*.

The state of the SAM after being exposed to oxygen radicals was assessed by a subsequent CV run in the anodic range under the conditions of Fig. 1. It was found *(Fig. 3b)* that the anodic desorption shifted by 0.2 V in the positive direction, relative to the CV run with a genuine carotenoid SAM (*Fig. 1).* The reason for such a change may be an increase in SAM stability, probably arising from cross-linking reactions induced by oxygen radicals.

(v) The chemical sate of the adsorbate

It is obvious from the previous results that the adsorption of the thione (**I**) generates a rather stable SAM on the gold surface and the SAM shows the particular features of chemisorption via a sulfur anchor. The question is whether the carbon-sulfur double bond in thione (**I**) is preserved after being adsorbed at the gold surface. As far as it is known, SAM formation by sulfur derivatives is an oxidative process with respect to gold [1]. In the typical case of alkane thiol adsorption, the electron acceptor could be either dissolved oxygen or the hydrogen ion in the thiol group.

The situation is very different for a non-saturated thione function, which might be the actual electron acceptor under such circumstances. The primary product of thione (**I**) adsorption on gold could be a radical (Formula **(II**) in Scheme 1), where the sulfur atom turned into the thiol state as a result of the electron uptake from gold. This assumption is supported by the absence of any characteristic electrochemical reaction of thiones, as described in ref. [20]. In the transient species (**II**), the unpaired electron is delocalised. A consequence of delocalisation is an enhanced freedom to rotate around the carbon-carbon bonds in the polyenic chain [21]. This would allow the adsorbed molecules to adopt a nearly perpendicular orientation to the substrate surface and, consequently, the surface layer would acquire a compact structure, in accord with the data on the surface blocking effect. The radical **(II**) is susceptible of a nucleophilic attack by water molecules, particularly at the 4' site, where such a reaction is stimulated by the combined effect of an increased electron density [22] and the direct contact with the aqueous solution. Therefore, the radical (**II**) may rearrange to a thiolate having a conjugated polyene system starting away from the sulfur-bounded carbon (Formula **(III**) in Scheme 1).

4. Conclusions

The carotenoid thione derivative **(I**) adsorbs on the gold surface and generates a SAM, which probably consists of form **(III**). The surface layer is electrochemically stable within the potential region between 0.5 and -0.6 V vs. SCE. However, an anodic reaction occurs at 0.9 V vs. SCE (peak A), consisting of an electron transfer from the conjugated polyene chain. The product of this process desorbs at even more positive potentials (peak B) simultaneously with gold oxide formation. Cathodic desorption in an alkaline solution occurs much more slowly.

Despite the size of the adsorbate molecule, the carotenoid SAM shows some notable differences when compared with a long chain alkane thiol SAM, particularly, the occurrence of the anodic desorption in an acidic solution and the absence of a marked cathodic desorption peak in an alkaline medium. Such differences may arise from the higher electron density in the non-saturated adsorbate molecule. It is obvious that the peak B originates from the reactive character of the carotenoid as an electron donor.

Results in this paper demonstrate the possibility of using sulfur derivatives of naturally occurring and commercially available carotenoids for preparing direct contacts between a metal support and long chain polyconjugated molecules, with potential applications as molecular wires.

References

[1] A. Ulman, Chem. Rev. 96 (1996) 1533.

[2] H. Finklea, in: A. J. Bard, I. Rubinstein (Eds.) Electroanalytical Chemistry, vol. 19, Marcel Dekker, New York, 1996, p. 109.

[3] D. Mandler, I. Turyan, Electroanalysis 8 (1996) 207.

[4] F. Schreiber, Progr. Surf. Sci. 65 (2000) 151.

[5] J. Roncali, Acc. Chem. Res. 33 (2000) 147.

[6] J.M. Tour, Acc. Chem. Res. 33 (2000) 791.

[7] G. Leatherman, E.N. Durantini, D. Gust, T.A. Moore, A.L. Moore, S. Stone, Z. Zhlu, P. Rez, Y. Z. Liu, S. M. Lindsay, J. Phys. Chem. B 103 (1999) 4006.

[8] D.Z. Liu, Y.L. Gao, L.D. Kispert, J. Electroanal. Chem. 488 (2000) 140.

[9] J. Heinze, P.Tschuncky, A. Smie, J. Solid State Electrochem. 2 (1998) 102.

[10] V.G. Mairanovsky, A.A. Engovatov, N.T. Ioffe, G.I. Samokhvalov, J. Electroanal. Chem. 66 (1975) 123.

[11] Z.F. He, L.D. Kispert, J. Phys. Chem. B 103 (1999) 9038.

[12] H.R. Sliwka, S. Liaaen-Jensen, Acta Chem. Scand. 48 (1994) 679.

[13] H. Angerstein-Kozlowska, B.E. Conway, B. Barnett, J. Mozota, J. Electroanal. Chem. 100 (1979) 417.

[14] J. Heyrovsky, J. Kuta, Principles of Polarography, Academic Press, 1966, p. 105.

[15] T. Iwasita, W. Schmickler, J. Herrmann, U. Vogel, J. Electrochem. Soc. 130 (1983) 2026.

[16] T. Iwasita, W. Schmickler, J. W. Schultze, Ber. Bunsen-Ges. Phys. Chem. 89 (1985) 138.

[17] I. Markovich, D. Mandler, J. Electroanal. Chem. 484 (2000) 194.

[18] A. Mortensen, L. H. Skibsted, T. G. Truscott, Archiv. Biochem. Biophys. 385 (2001) 13.

[19] D. T. Sawyer, A. Sobkowiak, J. L. Roberts, Jr., Electrochemistry for Chemists, J. Wiley, New York, 1995, p. 358.

[20] J. Q. Chambers, in: A. J. Bard, H. Lund (Eds.), Encyclopedia of Electrochemistry of the Elements, Vol. 12, Marcel Dekker, New York, 1978, p. 329.

[21] W. von Doering, T. Kitagawa, J. Am. Chem. Soc. 113 (1991) 4288.

[22] S. Liaaen-Jensen, in: O. Isler (Ed.), Carotenoids, Birkhäuser, Basel, 1971, p. 61.

FIGURE CAPTIONS

Figure 1. CV records at a carotenoid covered Au electrode (1 - first CV scan; 2 to 4 - subsequent scans) and at a bare Au electrode (5). Inset: multiple scan CV records at a SAM covered electrode in the potential region of the peak A. Supporting electrolyte: 10^{-2} M $HClO_4$; scan rate, 100 mV/s.

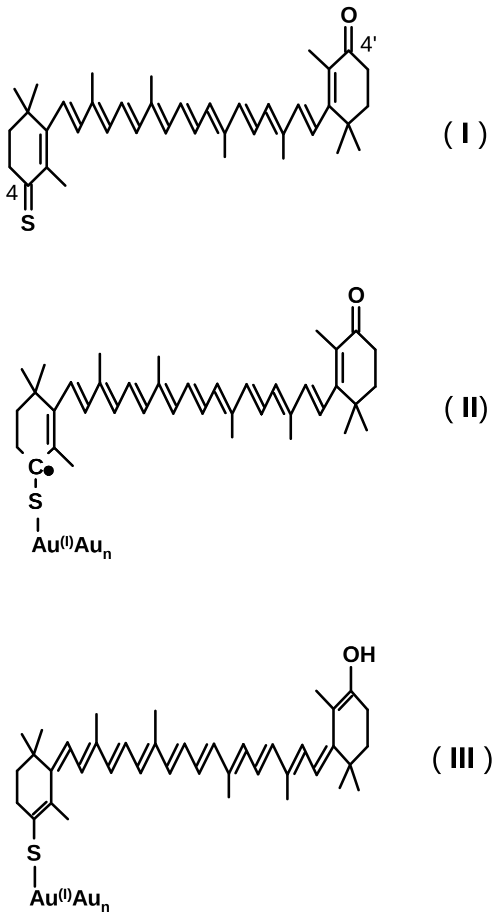
Figure 2. Effect of the carotenoid surface layer in cyclic voltammetry of (a) 5.10^{-3} M $[Fe(CN)_6]^{3-}$ and (b) 10^{-3} M $Ru(NH_3)_6{}^{3+}$, both in 0.1 M KNO_3. (1) Bare gold electrode. (2) and (3) SAM covered gold electrode. SAM formation time: (2) 25 min; (3) 55 min. Scan rate100 mV/s.

Figure 3. a. CV (at 100 mV/s) for oxygen reduction at a plain (1) or modified gold electrode (2-5), in $HClO_4$ 10^{-2} M. Only the direct scan is displayed. The modified electrode was submitted to a continuous potential cycling for 1 hour. Displayed: first scan (2); 2nd scan (3); 8th scan (4); and last scan (5). Scan rate, 100 mV/s.b. Anodic desorption of the carotenoid layer performed after cycling for 1 hour under the conditions of Fig. 3 a. Supporting electrolyte: $HClO_4$ 10^{-2} M. Scan rate, 100 mV/s.

Table 1.

Pinhole parameters for a carotenoid SAM as determined by means of either $[Fe(CN)_6]^{3-}$ or $[Ru(NH_3)_6]^{3+}$ as redox probes. R_a is the pinhole average radius; R_0 stands for the average half-distance between pinholes. Electrolyte: 0.1 M KNO_3; scan speed, 100 mV/s; modification time, 20 min. Constant values used in calculation for $[Fe(CN)_6]^{3-}$: $D = 7.4 \cdot 10^{6}$ cm^2/s [14], k^o = 0.38 cm/s [15]; for $[Ru(NH_3)_6]^{3+}$: $D = 6 \cdot 10^{-6}$ cm^2/s; k^o = 1 cm/s [16].

Redox probe	$1-\theta$	R_0 /µm	R_a /µm
5 mM $K_3[Fe(CN)_6]$	0.007	6.9	0.57
1 mM $[Ru(NH_3)_6]Cl_3$	0.003	2.9	0.17



Scheme 1

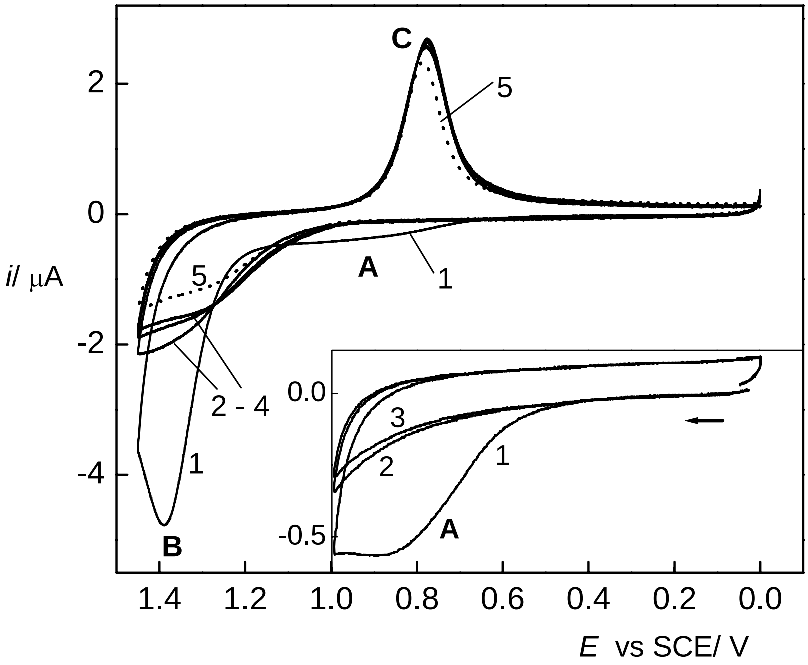
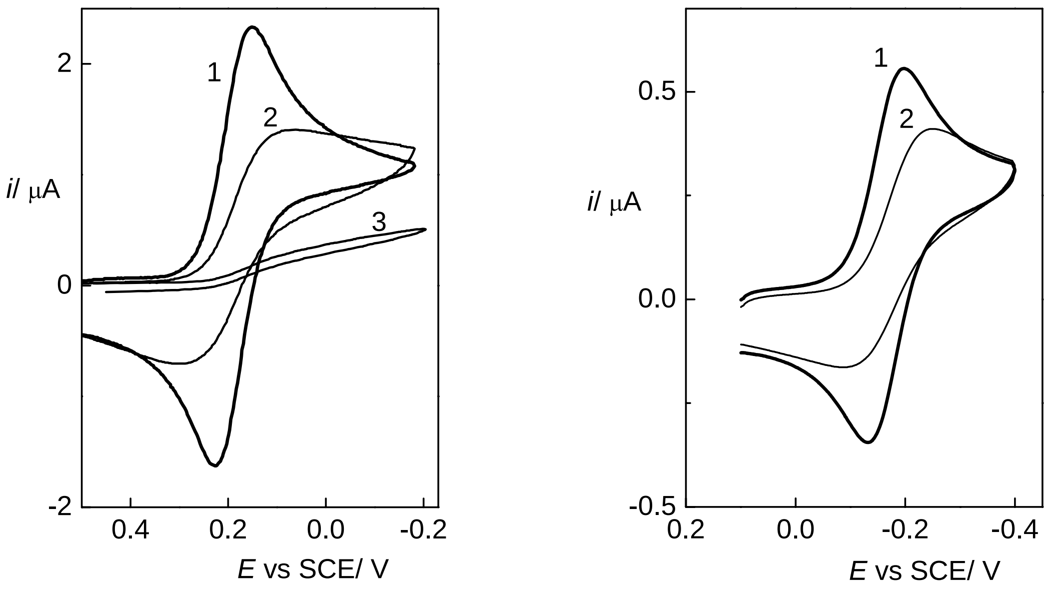
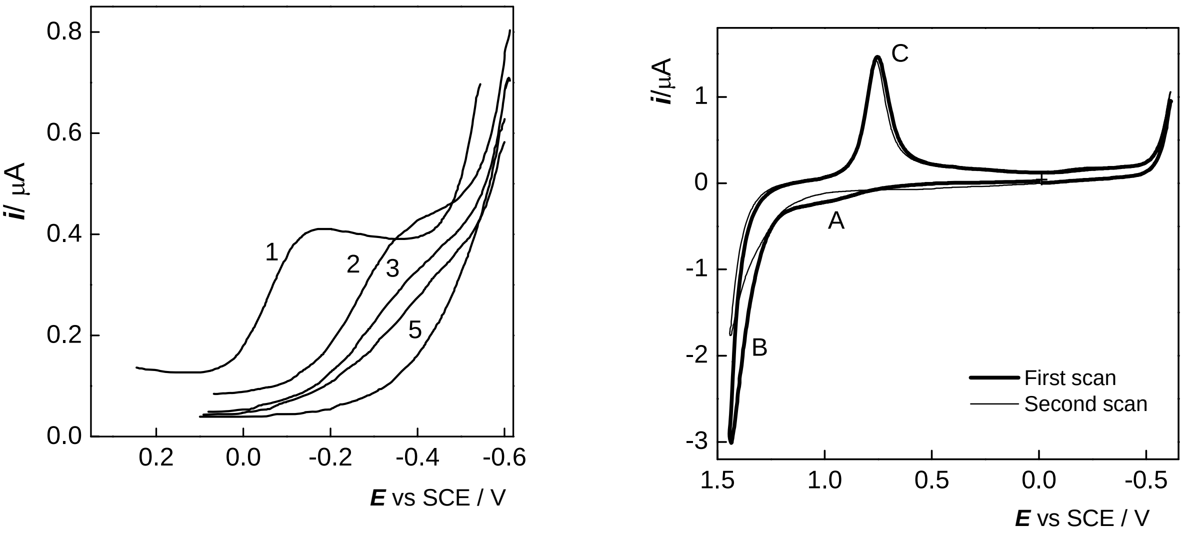


Figure 1



(a) **(b)**

Figure 2



(a) **(b)**

Figure 3