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Electrode reactions of palladium(II) in chloride solution at carbon paste electrodes modified with derivatives of *N*-benzoylthiourea

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Abstract The study of the electrode reactions of palladium(II) at non-modified carbon paste electrodes (CPEs) in chloride solution has revealed the existence of a chloropalladate(II) complex at the electrode surface. The complex is formed during the application of anodic potentials after preceding palladium deposition. In the present paper the electrode reactions of Pd^{II} at CPEs modified with some *N,N'*-disubstituted derivatives of *N*-benzoylthiourea [as selective ligands for palladium(II)] are studied in chloride solution by cyclic voltammetry. Two reduction peaks are observed in the cathodic scans recorded after deposition of palladium and anodization of the electrode. From the results it is concluded that [in addition to the chloropalladate(II) complex, observed at the non-modified electrode] a second palladium complex is formed at positive potentials. The formation of the palladium(II) complex of the *N*-benzoylthiourea derivatives by ligand exchange at the electrode surface is assumed. The ligand exchange itself occurs without charge transfer across the electrode|solution interface; therefore, it cannot be detected electrochemically. After palladium deposition and anodic treatment a pronounced “inverse” peak (i.e., an anodic peak in the cathodic scan) with peak currents up to 100 μ A is observed at about +0.8 V. Its peak current increases with the amount of deposited palladium and the number of cycles. The reactions at the electrode surface are discussed. The results of the study reveal the existence of two different surface complexes of palladium(II) at ligand-modified CPEs, but the surface reactions could not be elucidated in detail.

Keywords *N*-Benzoylthiourea · Carbon paste electrode · Chloride · Palladium · Surface complex

Introduction

Electrodes modified with selective ligands enable the immobilization of metal ions by the formation of surface complexes at the electrode [1, 2, 3]. The procedure is widely used for the pre-concentration of metals for analytical purposes, often by the usage of modified carbon paste electrodes (CPEs) [4]. The formation of silver(I) complexes at CPEs modified with 2,5,8-trithia[9]-*m*-cyclophane as ligand was studied recently [5].

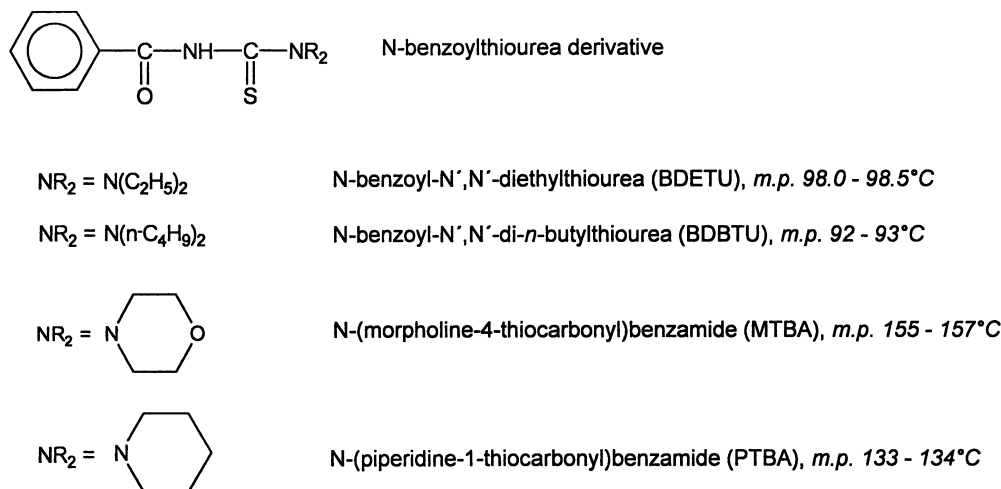
The immobilization of palladium and its compounds on solid surfaces is of interest because of their catalytic activity [6, 7]. Different procedures are employed, among them the electrolytic deposition on conducting substrates. The immobilization at carbon electrodes succeeds with tetrachloropalladate solutions [8, 9] by potentiostatic treatment or treatment at open circuit [8]. Immobilization of palladium at the surface of modified electrodes enables the electroanalytical determination of traces of palladium [2, 8, 10]. Recently, the formation of palladium-chloro complexes at the surface of non-modified CPEs was observed, concluded from the appearance of additional redox peaks after the preceding palladium deposition and anodic treatment [11]. Because of the formation of the palladium-chloro complex at the non-modified CPE, the question arises if the chloro complex (or the presence of the chloride ions) influences the reactions of Pd^{II} at electrodes modified with selective organic ligands.

For this reason we started a voltammetric study of Pd^{II} at CPEs modified with *N,N'*-disubstituted derivatives of *N*-benzoylthiourea (see Scheme 1) with potassium chloride as the supporting electrolyte. The *N*-benzoylthiourea (BTU) derivatives are selective complexing agents for thiophile metals and form palladium(II) complexes of high stability [12, 13], which are sparingly soluble in water and used for the

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Scheme 1. Derivatives of *N*-benzoylthiourea used as modifying agents



determination of traces of palladium by means of atomic absorption spectrometry [14]. Furthermore, BTU derivatives were utilized for the modification of CPEs in order to immobilize silver(I) [15]. Therefore, *N'*,*N'*-disubstituted BTU derivatives should be suitable for the modification of electrodes in order to immobilize palladium(II) at the electrode surface.

In the present work the reactions of Pd^{II} at a ligand-modified electrode in the presence of chloride as a complexing anion are studied by cyclic voltammetry (CV). Furthermore, the possibility for the immobilization of palladium at the electrode surface by means of BTU derivatives will be checked, where in particular the formation of surface complexes of Pd^{II} at the electrode is of interest. Palladium surface complexes are of importance in catalytic reactions because reversible redox reactions of surface complexes enable the “electrochemical recycling” of Pd complexes [16, 17]. Furthermore, the results are of interest for the electroanalytical determination of palladium at modified electrodes in chloride-containing solutions.

Experimental

As the working electrode, a CPE with 8 mm diameter for the active electrode area (no. 6.0802.000, Metrohm, Germany) was used. A silver/silver chloride electrode in saturated KCl (SE 10) served as the reference electrode and a Pt electrode (MC 20, both from Sensortechnik Meinsberg, Germany) as the counter electrode. All potentials are referred to the Ag/AgCl electrode. The carbon paste consisted of graphite powder (RW-B, Ringsdorf, Bonn-Bad Godesberg, Germany), paraffin oil (Uvasol, Merck, Darmstadt, Germany) and additions of 20–25% of the BTU derivative (with respect to the total mass of the carbon paste). The components were thoroughly mixed in an agate mortar and the electrode surface smoothed on a Teflon plate.

A stock solution of 4×10⁻³ M tetrachloropalladate was prepared from Na₂[PdCl₄] (Bergbau- und Huettenkombinat, Freiberg, Germany) and 0.5 M KCl. KCl and HCl were purchased from Merck (Darmstadt, Germany), buffer solutions from Sensortechnik Meinsberg. Aqueous chloride solutions of different pH, made from 0.5 M KCl and additions of HCl, were used as supporting electrolyte. The solutions were deaerated with nitrogen.

Derivatives *N*-benzoyl-*N'*,*N'*-diethylthiourea (BDETU), *N*-benzoyl-*N'*,*N'*-di-*n*-butylthiourea (BDBTU), *N*-(morpholino-4-thiocarbonyl)benzamide (MTBA) and *N*-(piperidino-1-thiocarbonyl)benzamide (PTBA) were used as modifying agents (see Scheme 1). They were synthesized according to the procedure described by Hartmann and Reuter [18] and recrystallized from ethanol; melting points are given in Scheme 1.

Voltammograms were recorded with the potentiostat SI 1286 (Solartron-Schlumberger, Farnborough, UK) by means of the software “DC CorrWare” (Scribner, Charlottesville, Va., USA). A scan rate of 20 mV/s was used. CVs were recorded either immediately after renewing the electrode surface or after the pre-treatment.

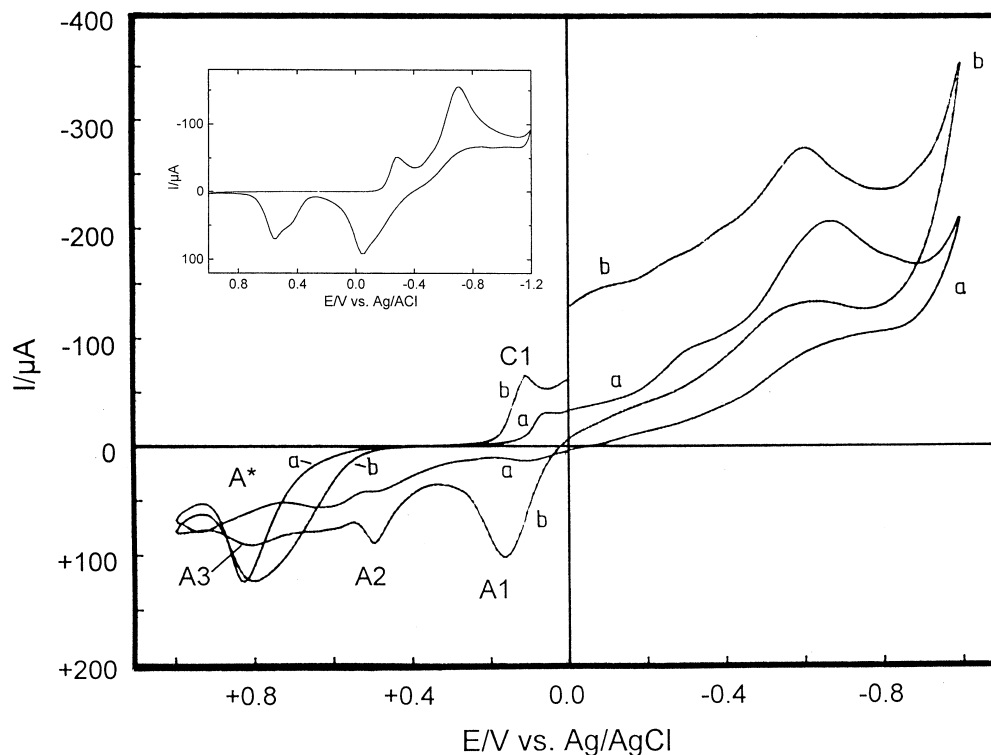
Results

At first, CVs of the CPE modified with derivatives of BTU were recorded in the supporting electrolyte. In cycles between -0.8 V and +1.0 V, no redox peaks were observed. After a preceding cathodic treatment (at $E \leq -0.9$ V) or a preceding cycle to corresponding potentials, a broad anodic peak with a maximum at about +0.4 V was observed. The anodic current is caused by the oxidation of the product from the reductive cleavage of the -CO-NH- group of the BTU derivative, as known from the study of the BTU derivatives at carbon electrodes (in ethanolic solution) [19].

Voltammograms obtained at a CPE modified with BDBTU in the presence of 1.8×10⁻⁴ M and 3.5×10⁻⁴ M Pd^{II} in the solution are shown in Fig. 1. Besides two anodic peaks (A1, A2) at +0.15 V and +0.5 V, a small anodic current at +0.8 V (A3) and the “inverse” anodic current A* appear at about +0.80 V in the scan to negative potentials. Furthermore, the cathodic peak C1 at about +0.1 V is noticeable. The anodic currents depend strongly on the preceding cycle or the pre-treatment. In CVs recorded without pre-treatment or preceding cycles to negative potentials, no anodic currents are observed in the range from +0.2 V to +1.0 V. The CV of [PdCl₄]²⁻ at the non-modified CPE is shown for comparison (inset of Fig. 1).

Cycling leads to alterations in particular of the anodic part of the voltammograms. For example, three cycles

Fig. 1. CVs of (a) 1.8×10^{-4} M Pd^{II} and (b) 3.5×10^{-4} M Pd^{II} at a CPE modified with 22% BDBTU (with respect to the total mass of the carbon paste). Supporting electrolyte 0.5 M $\text{KCl} + 1 \times 10^{-3}$ M HCl ($\text{pH} \approx 3.0$). Cycles from 0 V to -1.0 V, $+1.0$ V and return. Scan rate 20 mV/s. CPE surface renewed before (a). *Inset:* CV of 1.6×10^{-4} M Pd^{II} at a non-modified CPE. Supporting electrolyte 0.5 M $\text{KCl} + 1 \times 10^{-3}$ M HCl ($\text{pH} \approx 3.0$). Cycle from $+0.25$ V to -1.2 V, $+1.0$ V and return. Scan rate 20 mV/s



recorded at the CPE modified with PTBA in the presence of 5×10^{-4} M Pd^{II} are shown in Fig. 2. Characteristic features are the two small oxidation currents (A2 and A3) and the remarkable increase of the “inverse” anodic current A^* with the number of cycles.

At the non-modified CPE, pre-treatment at potentials $E \leq +0.2$ V causes one or two oxidation peaks in the subsequent cycle. The anodic currents are caused by the oxidation of Pd^0 deposited during the pre-treatment, where the two oxidation peaks are attributed to the dissolution of a Pd^0 monolayer (or sub-monolayer respectively) and the palladium multilayer [11, 20]. In the present study, corresponding experiments were conducted at a CPE modified with BTU derivatives. Even pre-treatment for some minutes causes an appreciable increase of the oxidation current A2 in subsequent cycles; longer treatment leads then to the appearance of two reduction currents. For example, after 90 minutes pre-treatment at open circuit, a peak current of 1.6 mA at $E_p = +0.57$ V (A2) and a small anodic current at $+0.12$ V (A1) are observed in the first cycle, besides the two cathodic peaks at $+0.17$ V (C2) and -0.01 V (C1), as shown in Fig. 3. The large half-width of peak A2 [e.g., $\Delta E(I_p/2) = 0.15$ V in Fig. 3] in contrast to the non-modified electrode is remarkable. The “inverse” anodic current A^* at about $+0.8$ V seems to be smaller, as in other CVs. However, the current is of the same order (peak current of about $+80$ μA); different current scales cause the apparent difference.

Cycling after preceding treatment causes the increase of the redox currents A1 and C1 and the simultaneous decrease of peaks A2 and C2 (see Fig. 5). The appear-

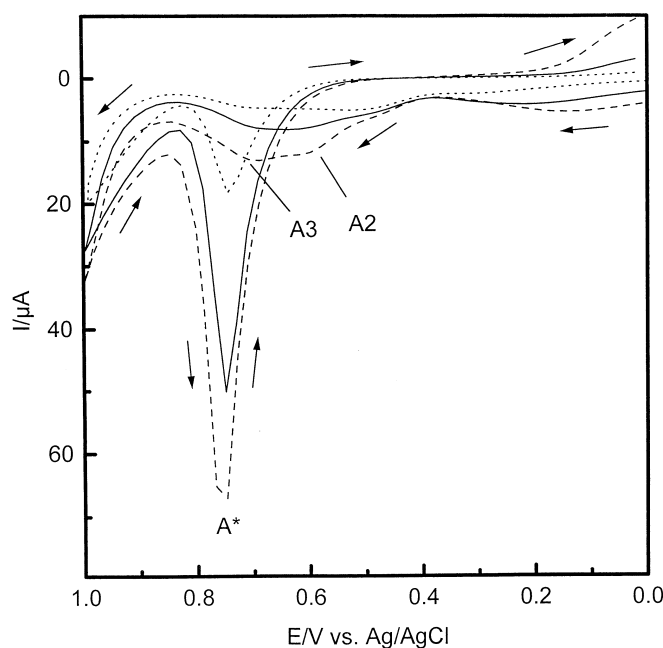


Fig. 2. Part of the CVs of 5×10^{-4} M Pd^{II} at a CPE modified with 20% PTBA (with respect to the total mass of the carbon paste). Supporting electrolyte 1.0 M $\text{KCl} + \text{HCl}$ ($\text{pH} 4.0$). Three cycles at the same CPE surface (with a stop after each cycle). Cycles from 0 V to -1.0 V, $+1.0$ V and return. Scan rate 20 mV/s. *Dotted line:* first cycle; *solid line:* second cycle; *dashed line:* third cycle

ance of the two cathodic peaks as well as the alterations during cycling lead to the assumption that different redox couples are formed at the modified electrode.

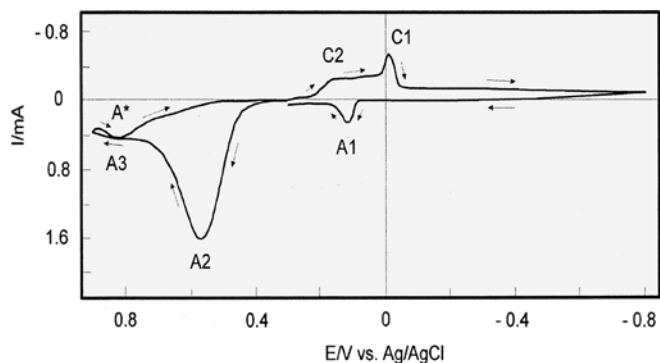


Fig. 3. CV of a CPE modified with 23% MTBA (with respect to the total mass of the carbon paste) after 90 min pre-treatment (at open circuit with stirring) in the presence of 4×10^{-5} M Pd^{2+} . Supporting electrolyte 0.5 M KCl, pH 5.5. Cycle from +0.3 V to +0.9 V, -0.8 V and return to +0.3 V (recorded after two cycles at the new surface and pre-treatment). Scan rate 20 mV/s

The influence of the pre-treatment time is shown in the next figure, where the CVs of 8×10^{-5} M Pd^{II} at the modified CPE were recorded (at the same electrode surface) after 2.5, 5, 10 and 15 minutes of pre-treatment (Fig. 4). After short pre-treatment, two small anodic currents (A2 and A3) are observed, whereas the drastic increase of peak A2 and the two distinct cathodic peaks are typical for CVs after longer pre-treatment. The “inverse” anodic current A^* appears also, but seems to be small for the same reason as in the preceding figure.

The result is confirmed by repeated experiments with different palladium concentrations. Three cycles recorded at the modified CPE in the presence of 1.2×10^{-4} M $[\text{PdCl}_4]^{2-}$ after 15 minutes pre-treatment at open circuit are shown in Fig. 5. Here, the anodic peak A1 is more pronounced than in the preceding figures, possibly because -0.3 V is chosen as the negative reversal potential.

The “inverse” anodic current A^* is also observed after pre-treatment at open circuit and solution exchange (exchange of the palladium-containing solution by the supporting electrolyte). Therefore, it is concluded that the current A^* is caused by a surface reaction. When the modified CPE is pre-treated at open circuit with stirring in presence of Pd^{II} , e.g. for more than 10 min with $\geq 4 \times 10^{-5}$ M palladium(II), a yellowish precipitate is observed at the electrode surface. The composition of the precipitate could not be elucidated; presumably a palladium(II) complex of the BTU derivative is formed.

Discussion

The system under study comprises palladium in the oxidation states +2 and 0, chloride ions (in solution) as well as the BTU derivative (on the electrode surface) as possible ligands for the palladium(II). The modified electrode consists of the carbon, the paraffin oil and the BTU derivative as modifying agent. Therefore, different

reactions are to be expected at the two phases of the “heterogeneous” electrode surface (consisting of the “carbon phase” and the “ligand phase”) as redox reactions at the carbon phase and surface reactions at the ligand phase without charge transfer across the electrode|solution interface. Since palladium is deposited at potentials negative to +0.2 V [11, 20], Pd^0 at the electrode surface has also to be considered. This means that the carbon surface changed (at least partly) to a palladium electrode after cathodic cycles, potentiostatic treatment at potentials $E < +0.2$ V or treatment at open circuit.

Voltammograms of tetrachloropalladate(II) at the non-modified CPE

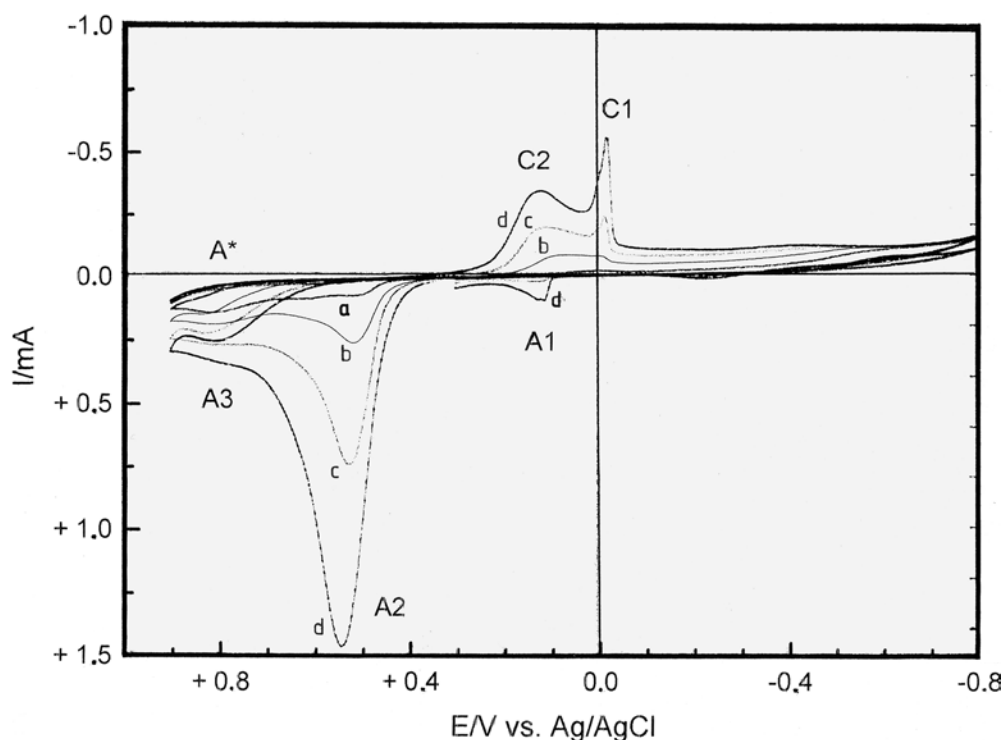
Palladium(II) forms in chloride solution (chloride concentration ≥ 0.5 M) predominantly the tetrachloropalladate complex $[\text{PdCl}_4]^{2-}$ [23]. At the non-modified CPE a pronounced oxidation peak (designated as A2) appears at about +0.5 V after preceding palladium deposition (by treatment at open circuit or potentials more negative than +0.2 V) [8]. The peak current of A2 increases at the non-modified electrode about linearly with the pre-treatment time and the palladium(II) concentration of the solution [8]. Furthermore, an additional oxidation peak at about +0.1 V is observed when low amounts of palladium are deposited, presumably caused by a palladium monolayer [11, 20].

After deposition of Pd^0 and anodic treatment (at $E \geq +0.9$ V) or cycling to corresponding potentials, an additional cathodic peak is observed at about 0 V and a corresponding anodic peak at +0.1 V, caused by a palladium-chloro complex formed during the anodic treatment at the electrode surface [11]. The voltammetric behaviour of the non-modified CPE in the presence of $[\text{PdCl}_4]^{2-}$ in the range of negative potentials is described in a preceding paper [21]. A CV recorded at the non-modified CPE is shown in the inset of Fig. 1.

Voltammograms of tetrachloropalladate(II) at the CPE modified with N',N' -disubstituted BTU derivatives

The characteristic features of the CVs recorded at the modified electrode are the two cathodic peaks C1 and C2 and the peak or current A3 and the “inverse” peak A^* in the anodic scan, besides the peaks A1 and A2 which appear at the non-modified CPE as well. Furthermore, the pronounced oxidation peak at 0 V (cf. inset of Fig. 1), which is caused by the oxidation of hydrogen sorbed at the deposited palladium [21], disappears at the modified CPE. This is presumably attributed to the modifier BTU, since the addition of thiourea to the electrolyte impedes the sorption of hydrogen at palladium [22]. C2 appears only after the preceding deposition of large amounts of Pd^0 (when the

Fig. 4. CVs of a CPE modified with 23% MTBA (with respect to the total mass of the carbon paste) in the presence of 8×10^{-5} M Pd^{2+} . Supporting electrolyte 0.5 M KCl, pH 5.5. Cycles from +0.3 V to +0.9 V, -0.8 V and return. CVs recorded after (a) 2.5, (b) 5, (c) 10 and (d) 15 min pre-treatment at open circuit (with stirring) at the same CPE surface. After each pre-treatment, one cycle was recorded. Scan rate 20 mV/s



product of the palladium concentration and the pre-concentration time, $c \times t$, is about $\geq 0.1 \text{ mol L}^{-1} \text{ s}$), indicated by the corresponding large peak A2 (Figs. 3, 4, 5). A2 is caused by the oxidation of deposited Pd^0 under formation of the tetrachloropalladate(II) complex. Peaks C1 and A1 are the corresponding redox peaks of the palladium-chloro complex formed during anodic treatment at the carbon surface (cf. [11]).

The small anodic peak A3 with a round maximum appears at about +0.8 V (cf. Figs. 1, 4). Its peak height depends on the deposited palladium amount (cf. Figs. 1, 2), but to a considerable lower degree than peak A2. After the deposition of larger Pd amounts, peak A2 increases much more than A3 and becomes broader, so that only the comparably small anodic current A3 is observed (Figs. 3, 4). Both peak A3 and the broadening of A2 are not observed at the non-modified CPE.

The appearance of C2 indicates that at the modified electrode an additional reducible product is obviously formed, but the corresponding oxidation peak of C2 is not observed. Therefore, an additional reaction at potentials more positive than the E_p of A2 is assumed.

The features of the CVs are observed with all BTU derivatives used as modifying agents. The anodic and cathodic electrode reactions are discussed below in detail.

“Inverse” peak A*

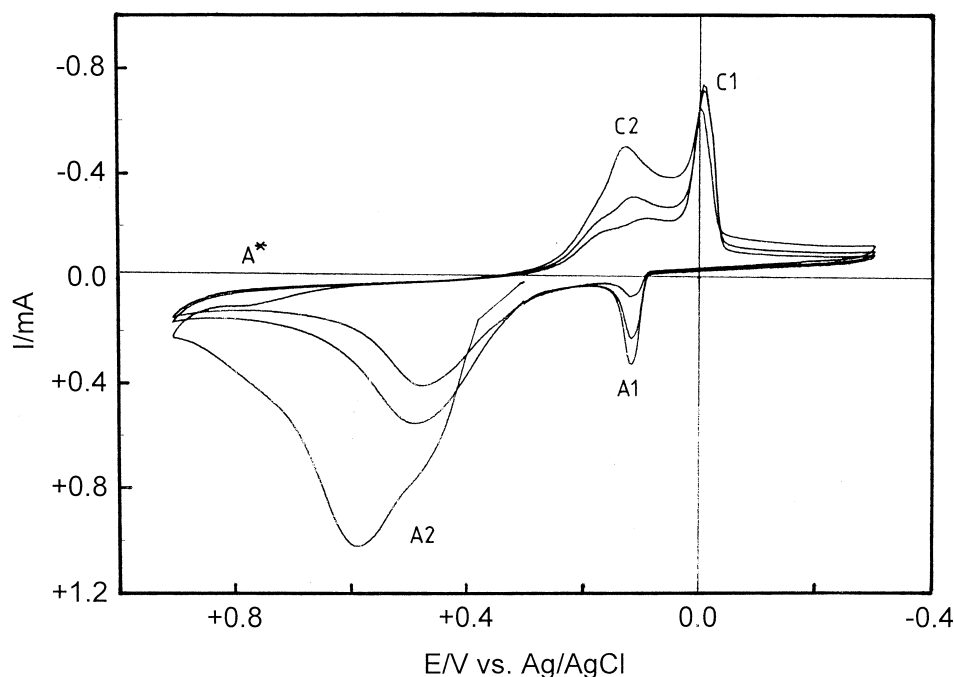
The “inverse” peak A* appears only after preceding palladium deposition (by treatment at open circuit or at negative potentials or cycles to negative potentials) and is

more pronounced in the case of low palladium coverage (Figs. 1, 2). Its peak height increases with the duration of the cathodic treatment or the number of cycles (Fig. 2). The “inverse” peak A* is not observed at low pH ($\text{pH} \approx 1$). Furthermore, it is either small or not observed when the CV is recorded without pre-treatment or without preceding cycles to negative potentials. Because the inverted peak is also observed after pre-treatment and subsequent exchange of the palladium-containing solution with the supporting electrolyte, it is obviously caused by a surface reaction.

A very small “inverse” current ($I_p < 2 \mu\text{A}$) is also observed at the non-modified CPE, but only in the first cycle after palladium deposition and subsequent treatment at potentials more positive than +0.9 V [11], whereas peak A* appears at the BTU-modified electrode in all cycles (after preceding palladium deposition) and its peak current is in the 10–100 μA range (cf. Figs. 1, 2).

“Inverse” peaks have been observed in different electrochemical systems. In the $\text{Ag}/\text{Ag}_2\text{O}/\text{OH}^-$ system, for instance, the appearance of an “inverted” peak is associated with the formation of higher oxidation states of silver at positive potentials [28]. Baldwin et al. [29, 30] described “inverted” peaks at electrodes modified with cobalt phthalocyanine in the presence of thiols and attributed the peaks as general phenomena in the electrocatalysis with these compounds. Furthermore, an “inverse” peak is observed in course of the catalytic oxidation of hydrazine at carbon electrodes coated with Au and Cu as catalysts [31]. Zhang et al. [32] observed an “inverse” reduction current in the course of the catalytic reduction of nitrite and nitric oxide at a graphite electrode modified with an iron-alizarin complex, where

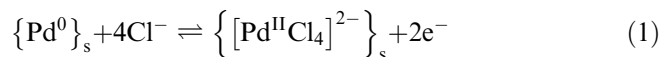
Fig. 5. CVs of a CPE modified with 23% MTBA (with respect to the total mass of the carbon paste) in the presence of 1.2×10^{-4} M Pd^{2+} . Cycles from +0.3 V to +0.9 V, -0.3 V and return. Scan rate 20 mV/s. Three cycles are recorded (without stop) after 15 min pre-treatment at open circuit (with stirring). Peaks A2 and C2 decrease during cycling, whereas peaks C1 and A1 increase



the formation of a surface compound of the reactant with the iron complex is assumed. "Inverse" peaks in voltammograms can also be attributed to electron transfer catalysis [33]. Here, the "inverse" peak is probably associated with surface reactions at the modified electrode in the presence of palladium(II).

Anodic electrode reactions

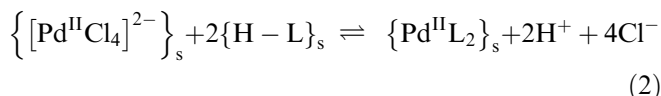
The peak current of A2 increases with the pre-treatment time (Fig. 4). Peak A2 is also observed at the non-modified CPE, but at the modified electrode very large peak currents (up to 1.5 mA) are recorded. As mentioned, the anodic current A2 is caused by the oxidative formation of a palladium-chloro complex according to Eq. 1 [8, 11]:



where the subscript *s* indicates surface-confined species. The deposited Pd^0 is not completely oxidized and remains partly at the electrode surface [8, 11], i.e. Eq. 1 proceeds until equilibrium is attained. The formed tetrachloropalladate(II) complex is at first sorbed at the electrode surface. Peak A2 is not observed in solutions without chloride (Lubert K-H, unpublished results).

The formation of the reducible species, which causes the peak C2, occurs in a further anodic reaction, presumably in the potential range of peaks A3 and A*. Since C2 is not observed at the non-modified electrode, it is concluded that the reaction occurs under participation of the BTU derivative. The $[\text{PdCl}_4]^{2-}$ formed according to Eq. 1 is adsorbed at palladium islands on the electrode surface. If its surface concentration increases, the

complex diffuses into the solution and/or moves on the electrode surface by surface diffusion. At the ligand region of the surface the $[\text{PdCl}_4]^{2-}$ complex can react with the BTU derivative H-L, e.g. according to Eq. 2:



where H-L is the BTU derivative (modifying agent) and the subscript *s* designates a surface-confined species again.

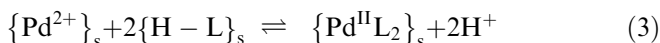
The $\text{Pd}^{\text{II}}\text{L}_2$ complex of the BTU derivative is considerably stronger than the chloro complex because of the chelating effect of the ligand L [13]. The stability of the Pd^{II} surface complexes at electrodes is not known, but their stability can be roughly estimated from the complex stability in solution [13, 23]. The stability constants ($\log \beta_2$) of complexes of Pd^{II} with derivatives of BTU are in the range from 37 to 40 in dioxane/water (75:25) and about 32 in aqueous solution [13], in contrast to the corresponding constant ($\log \beta_4$) for $[\text{PdCl}_4]^{2-}$ which is 11.5 [23].

The mechanisms of ligand exchange at the electrode surface could not be elucidated in detail. However, it is concluded that Eq. 2 occurs certainly in ligand regions of the surface and without electron transfer across the electrode/solution interface. Therefore, the surface diffusion of $[\text{PdCl}_4]^{2-}$ ions from the carbon region and/or palladium-coated sites to the "ligand region" of the surface is necessary. The ligand exchange causes also the release of protons (cf. Eq. 2), which diffuse into the solution. However, charge transfer across the ligand/solution interface causes no current, since the ligand region of the surface is not part of the electrode. Therefore, the ligand exchange reaction (Eq. 2) does not cause a redox current.

Because both current A3 and the “inverse” anodic current A* are not observed at non-modified electrodes (under the same experimental conditions), both currents are presumably connected with Eq. 2, for instance by direct or indirect influence on the equilibrium. Provided Eq. 2 occurs in the potential range of A3, $[\text{PdCl}_4]^{2-}$ is consumed and its surface concentration decreases. Then the formation of tetrachloropalladate(II) according to Eq. 1 is initiated, accompanied by an oxidation current.

Furthermore, the facilitation of the surface diffusion of $[\text{PdCl}_4]^{2-}$ is possible in this potential range, e.g. by weakening of the palladium-chlorine bond at positive potentials under the influence of the BTU ligand. It is reported that in the presence of suitable organic ligands (such as trithiacyclononane) the oxidation of Pd^{II} starts at about +0.60 V vs. Fc/Fc^+ (which corresponds to about +0.95 V vs. Ag/AgCl) and that a stable palladium(III) complex is formed [24]. BTU derivatives are oxidized at carbon electrodes at potentials more positive than +0.9 V [19], so that oxidation of the ligand can be excluded as the cause of the oxidation currents A3 and A*.

Besides Eq. 2, the $\text{Pd}^{\text{II}}\text{L}_2$ complex could also be formed by “direct” complex formation after the preceding oxidation of deposited palladium to Pd^{2+} , e.g. according to:



However, this reaction seems of minor probability, because palladium oxidation leads in chloride solution to the formation of the $[\text{Pd}^{\text{II}}\text{Cl}_4]^{2-}$ complex (Eq. 1) and the reaction occurs (according to the results presented) also at the modified CPE. Therefore, the existence of non-coordinated Pd^{2+} ions at the electrode surface is improbable, as is Eq. 3, which can only take place at the ligand region of the electrode surface and requires the surface diffusion of Pd^{2+} ions.

The “chlorination” of the carbon surface by the anodic reaction of chloride ions at carbon surfaces [25, 26] can also influence Eq. 2. An electrode reaction at potentials more positive than +0.8 V can be deduced from the increasing anodic currents (cf. Fig. 2). Therefore, the appearance of peak A* after the potential reversal could be attributed to the increase of the reaction rate of Eq. 2, caused by the “chlorinated” carbon surface and the faster surface diffusion of the tetrachloropalladate(II).

The currents A3 and A* appear at nearly the same potential (cf. Figs. 1, 2). According to the suggested mechanism, both currents are caused by the formation of $[\text{PdCl}_4]^{2-}$ according to Eq. 1, induced by the consumption of $[\text{PdCl}_4]^{2-}$ in the ligand exchange of Eq. 2. In acidic solutions ($\text{pH} \approx 1$), where the equilibrium of Eq. 2 shifts to the left side, the “inverse” peak A* as well as the reduction current C2 are not observed.

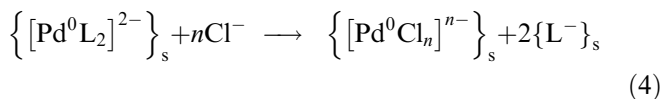
The formation of palladium(IV) species at positive potentials cannot be excluded, but it is improbable since the corresponding oxidation peak at glassy carbon and pyrolytic graphite (in chloride-containing solutions) is observed at +1.35 V (vs. SCE or $\text{Ag}/\text{AgCl}/\text{KCl}$, sat.)

[34, 35], whereas +0.9 or +1.0 V are used as the positive reversal potential in the present study.

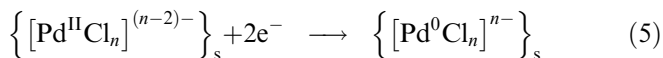
Cathodic electrode reactions

Peak C2 appears only after the deposition of large amounts of palladium and their oxidation to tetrachloropalladate(II), indicated by the corresponding oxidation currents A2. The surface concentration of the BTU ligand (H-L) is constant. Therefore, the formation of corresponding amounts of the $[\text{PdCl}_4]^{2-}$ complex is necessary in order to initiate the ligand exchange of Eq. 2. For this reason, the reduction peak C2 (reduction of the $\text{Pd}^{\text{II}}\text{L}_2$ surface complex) is not observed in the case of low Pd^0 coverage and low tetrachloropalladate(II) surface concentration.

Since the $\text{Pd}^{\text{II}}\text{L}_2$ complex is insoluble in aqueous solution, it exists as a surface complex which is reduced at C2, presumably to the corresponding palladium(0) complex $[\text{Pd}^0\text{L}_2]^{2-}$. However, an oxidation current of the Pd^0L_2 complex is not observed, because it is probably not stable. Cycling leads to the increase of peak C1 and the simultaneous decrease of C2 (cf. Fig. 4), indicating the different stability of the surface complexes and their mutual exchange, e.g. according to Eq. 4:



As indicated by the two reduction currents C2 and C1, at least two different palladium(II) complexes are formed at the modified CPE. Because C1 and A1 appear at the same peak potentials as the corresponding peaks at the non-modified electrode [11], it is concluded that C1 is caused by the reduction of the coexisting tetrachloropalladate(II) complex. Reduction of the tetrachloropalladate(II) at C1 leads probably to a chloropalladate(0) complex, e.g. according to Eq. 5:



provided that the corresponding palladium(I) complex is not formed (discussed later). The appearance of the corresponding oxidation peak A1 shows that the palladium(0) complex is rather stable (cf. [11]).

As mentioned, the reduction currents C1 and C2 appear only after deposition and re-oxidation of larger amounts of Pd^0 . The cathodic peak currents increase obviously with the increase of the redox charge exchanged in the scan to positive potentials (Fig. 4).

Palladium(I) complexes at electrodes

Two anodic peaks are often observed in the course of palladium oxidation at carbon electrodes. They are attributed to the oxidation of hydrogen, co-deposited with the palladium, and the Pd itself [27], the oxidation

of a Pd monolayer and a Pd multilayer [20] or the stepwise oxidation to Pd^{II} via palladium(I) at a CPE modified with sodium humate [10]. However, there is no experimental evidence for the existence of Pd^I. At modified electrodes, the formation of palladium(I) complexes at the electrode surface cannot be excluded, in particular in the presence of ligands which are able to stabilize unusual oxidation states. On the other hand, Pd^I tends to fast disproportionation into the more stable oxidation states 0 and +2. In the case under study, there are no indications for the formation of a Pd^I complex at the electrode. Palladium(I) complexes of BTU derivatives are not known.

Conclusions

The formation of palladium-chloro complexes at a non-modified CPE in chloride solution was found recently [11]. For this reason the electrode reactions of a CPE modified with *N,N'*-disubstituted derivatives of BTU (as selective ligands for the Pd^{II}) in chloride solution were studied by CV. After the deposition of Pd⁰ (by pretreatment at open circuit or at potentials near 0 V), two oxidation currents are observed in the range from +0.4 V to +0.9 V at the modified CPE, as well as two cathodic peaks in the subsequent scan to negative potentials. Furthermore, an "inverse" anodic peak is observed at +0.8 V in all cycles after preceding Pd⁰ deposition. From the experimental results the formation of two different complexes of palladium(II) during the cycle to positive potentials is concluded. In addition to the palladium(II)-chloro complex, observed at the non-modified CPE [11], the formation of a palladium(II) complex Pd^{II}L₂ with the organic ligand H-L is suggested. The complex formation occurs probably via a ligand exchange reaction at the electrode surface, a reaction without charge transfer across the electrode/solution interface. Therefore, the elucidation of the reaction mechanism by electrochemical means is difficult.

The present study reveals the co-existence of two surface complexes of palladium(II) at the electrode in the presence of chloride ions and the BTU derivative H-L as competing ligands. The reaction mechanism is of importance for the analytical utilization of ligand-modified CPEs, e.g. for the determination of palladium(II) in chloride media [10].

The suggested mechanism is in accordance with the experimental results, but the conclusions are predominantly drawn by comparison with the corresponding results obtained at a non-modified electrode in the presence of chloride. Possible reactions of palladium(II) solution species with the ligand, with complex formation at the surface during treatment at open circuit, have not received much attention. In order to obtain better insight into the electrode and surface reactions of the system under study, additional experiments are necessary, e.g. with palladium(II) at the electrode mod-

ified with BTU derivatives in the absence of chloride and other coordinating anions.

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References

1. Abruna H (1988) *Coord Chem Rev* 86:133
2. Raber G, Kalcher K, Neuhold CG, Talaber C, Kölbl G (1995) *Electroanalysis* 7:138
3. Zhang J, Lever ABP, Pietro WJ (1995) *J Electroanal Chem* 385:191
4. Kalcher K, Kauffmann JM, Wang J, Svancara I, Vytras K, Neuhold C, Yang Z (1995) *Electroanalysis* 7:5
5. Lubert KH, Beyer L, Casabó J, Pérez-Jiménez C, Escriche L (1999) *J Electroanal Chem* 475:73
6. Tsui J (1997) *Palladium reagents and catalysts*. Wiley, Chichester
7. Gurrath M, Kuretzky T, Boehm HP, Okhlopko LB, Lisitsyn AS, Likhohobov VA (2000) *Carbon* 28:1241
8. Lubert KH, Guttman M, Beyer L (1996) *Electroanalysis* 8:320
9. Simonov PA, Romanenko AV, Prosvirin IP, Moroz EM, Boronin AI, Chuvilion AL, Likhohobov VA (1997) *Carbon* 35:73
10. Sun Q, Wang C, Li L, Li H (1999) *Fresenius J Anal Chem* 363:114
11. Lubert KH, Guttman M, Beyer L (2001), *Collect Czech Chem Commun* 66:1457
12. Beyer L, Hoyer E, Hennig H, Kirmse R, Hartmann H, Liebscher J (1975) *J Prakt Chem* 317:829
13. Schmidt S, Dietze F, Hoyer E (1991) *Z Anorg Allg Chem* 603:33
14. Schuster M, Schwarz M (1996) *Anal Chim Acta* 328:1
15. Guttman M, Lubert KH, Beyer L (1996) *Fresenius J Anal Chem* 356:263
16. Armatore C, Jutand A, Medeiros MJ, Mottier L (1997) *J Electroanal Chem* 422:125
17. Armatore C, Jutand A (2000) *Acc Chem Res* 33:314
18. Hartmann H, Reuter I (1973) *J Prakt Chem* 315:144
19. Lubert KH, Beyer L, Guttman M (1999) *Collect Czech Chem Commun* 64:1937
20. Lubert KH, Guttman M, Beyer L, Kalcher K (2001) *Electrochim Commun* 3:102
21. Lubert KH, Guttman M, Beyer L (1999) *J Electroanal Chem* 462:174
22. Han JN, Pyun SI, Yang TH (1997) *J Electrochem Soc* 144:4266
23. Elding LI (1972) *Inorg Chim Acta* 6:647
24. Blake AJ, Holder AJ, Hyde TI, Schröder M (1987) *J Chem Soc Chem Commun* 987
25. Dunsch L, Inzelt G, Horanyi G, Lubert KH (1989) *J Electroanal Chem* 260:495
26. Dunsch L, Inzelt G, Horanyi G, Lubert KH (1990) *Isotopenpraxis* 26:343
27. Kiryushov VN (1998) *Ind Lab* 64:702
28. Stonehart P (1968) *Electrochim Acta* 13:1789
29. Halbert MK, Baldwin RP (1985) *Anal Chem* 57:591
30. Qi X, Baldwin RP (1996) *J Electrochem Soc* 143:1283
31. Jannakoudakis AD, Jannakoudakis PD, Pagalos N, Theodoridou E (1994) *Electrochim Acta* 39:1881
32. Zhang J, Lever ABP, Pietro WJ (1994), *Inorg Chem* 33:1392
33. Amatore C, Pinson J, Saveant JM (1980) *J Electroanal Chem* 107:74
34. Li F, Zhang B, Wang E, Dong S (1997) *J Electroanal Chem* 422:27
35. Li F, Zhang B, Dong S, Wang E (1997) *Electrochim Acta* 42:2563