

FORMATION OF PALLADIUM COMPLEX AT CARBON PASTE SURFACE IN CHLORIDE SOLUTION AS STUDIED BY CYCLIC VOLTAMMETRYKarl-Heinz LUBERT^{a1,*}, Markus GUTTMANN^b and Lothar BEYER^{a2}

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The deposition and dissolution of palladium at non-modified carbon paste electrode (CPE) is studied by cyclic voltammetry in chloride solutions ($c \geq 0.5$ M KCl and pH 3 to 6). The Pd⁰ is deposited from tetrachloropalladate solution by potential cycles from $E \geq 0$ V (vs Ag/AgCl) or positive potentials up to -0.5 V or by potentiostatic treatment at $E \leq 0$ V. Oxidation peaks appear during potential sweep to positive direction after the preceding deposition of Pd. The appearance of two anodic peaks depends mainly on the amount of Pd⁰ deposited. The peak at about $+0.1$ V is caused by the dissolution of a palladium mono- or submonolayer, whereas the oxidation peak at more positive potentials is attributed to the dissolution of Pd from a palladium multilayer. After palladium deposition and potential sweep to positive potentials $E > +0.8$ V (or potentiostatic treatment at $E > +0.8$ V), a cathodic peak appears at about 0 V and corresponding anodic peak at $+0.1$ V. It is concluded that these peaks are caused by reduction and oxidation of the chloropalladate surface complex formed during preceding application of anodic potentials. Reaction schemes of Pd^{II}/Pd⁰ and chloropalladate complex are discussed.

Keywords: Anodic oxidation; Electroreduction; Carbon electrode; Electrodeposition; Surface complexes; Tetrachloropalladate; Electrochemistry; Supported palladium catalysts.

The modification of solid surfaces with palladium is of great importance because of the catalytic potential of palladium and its compounds^{1,2}. The unique catalytic efficiency of palladium and the application of carbon substrates stimulated many studies concerning the modification of carbon surfaces by palladium and palladium compounds³⁻¹⁷, the interfacial chemistry of palladium electrodes¹⁸ as well as the application of palladium-modified surfaces in catalysis², electrochemistry^{3,10} and analytical chemistry⁵⁻⁹.

Carbon is the preferred support for palladium catalysts^{19,20}. Therefore, the electrochemical deposition of Pd on carbonaceous materials is a suit-

able method for preparation of Pd catalysts. But electrochemical studies of palladium(II) at carbon electrodes are often directed to analytical purposes or hydrogen sorption on Pd, whereas details of its deposition and dissolution processes on carbon electrodes seem to be of minor interest.

This is in contrast to detailed investigations of deposition and dissolution of palladium at single crystal electrodes of noble metals (Au, Pt)²¹⁻²⁵. The studies reveal an important role of halide ions and tetrahalide complexes of Pd^{II} in electrode reactions. In chloride solution the adsorption of [PdCl₄]²⁻ at the electrode surface is found to be the initial step of the deposition of Pd⁰ and the dissolution is regarded as a halide-induced or halide-catalysed reaction with the formation of adsorbed halide complexes of Pd^{II}. Furthermore, it is observed that the anodic dissolution of Pd from Pd(110) surfaces occurs only in presence of chemisorbed iodine. The anodic reaction is described as adsorbate-catalysed dissolution²³ and the interactions of halides with the Pd surface were found to follow the homogeneous coordination chemistry of palladium(II)-halo complexes²⁶.

Carbon paste electrodes (CPE) are used as support for Pd (refs^{5,27}) because of their renewable electrode surface and the possibility of modifying the electrode simply by addition of relevant agent to the carbon paste²⁸. CPE are widely used in electroanalytical chemistry^{29,30} and being advantageous for the study of the surface coordination of metal ions at ligand-modified electrodes³¹. According to recent experimental results, Pd can be immobilised at carbon paste electrodes by cathodic deposition, by pre-treatment at 0 V vs Ag/AgCl or under open circuit conditions^{27,32}. In chloride solution, Pd⁰ is then oxidised at about +0.5 V (vs Ag/AgCl), which enables electroanalytical determination of palladium(II). Some peculiarities connected with the deposition of palladium at CPE were mentioned by Adekola *et al.*³³ and were also observed by us at low Pd^{II} concentrations²⁷. The existence of different states of palladium(0) at the surface of carbon paste electrodes was described very recently³⁴; they are attributed to the formation of a Pd⁰ monolayer and multilayer in dependence of the deposited palladium amount.

In the present paper the deposition of palladium(0) from [Pd^{II}Cl₄]²⁻ solution is studied at the non-modified CPE by cyclic voltammetry (CV) in the potential range from -0.5 to +1.2 V vs Ag/AgCl at concentration of Pd^{II} ranging from 1 · 10⁻⁷ to 1 · 10⁻⁴ mol l⁻¹ and the chloride concentration ≥ 0.5 mol l⁻¹. Chloride is used as supporting electrolyte due to the important influence of halide ions on the deposition of Pd⁰ on other substrates^{18,22-25}. Cyclic voltammograms are recorded after deposition of Pd⁰ by preceding treatment at negative potentials or pre-treatment under open circuit condi-

tions. Furthermore, the influence of cycling or potentiostatic treatment at potentials more positive than +0.8 V was studied after preceding palladium deposition. The anodic treatment of carbon electrodes leads to the formation of oxidised surface groups and, in chloride solution, to the formation of carbon-chlorine bonds^{35,36}.

The results will contribute to palladium deposition and dissolution mechanisms at carbon substrates in chloride solution. The knowledge of the voltammetric behaviour of Pd^{II} and Pd⁰ at non-modified carbon electrodes is the precondition for corresponding studies at modified CPE, where, in particular, the formation of surface complexes of Pd^{II} is of interest^{37,38}. The results could expand the applicability of palladium-modified CPE, *i.e.*, "renewable" palladium electrodes for catalytic and electroanalytical purposes.

EXPERIMENTAL

The 3-electrode electrochemical cell was equipped with commercially available carbon paste electrode (diameter of the active area 8 mm; No. 6.0820.000, Metrohm, Filderstadt, Germany) as a working electrode, platinum electrode (MC 20) as a counter electrode and Ag/AgCl/KCl(sat.) (SE10) or SCE (KE 10, all from Sensortechnik Meinsberg, Germany) as reference electrodes. The Ag/AgCl/KCl(sat.) reference electrode is used except of experiment illustrated in Fig. 1 and the inset, where SCE was used. Carbon paste consists of 5.0 g of graphite powder (RW-B, Ringsdorff, Bonn-Bad Godesberg, Germany) with an average particle size of 5–10 μm (ref.²⁹) and of 2.25 g (about 2.0 ml) paraffin oil (Uvasol®, Merck, Darmstadt, Germany) thoroughly mixed in an agate mortar. The glass cylinder of the working electrode was filled with carbon paste. The electrode surface was smoothed on a Teflon plate in order to improve the surface reproducibility. The surface was renewed after each measurement unless otherwise stated.

Stock solutions of $1 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$ M sodium tetrachloropalladate in 0.5 or 1.0 M KCl were prepared. Several microliters of stock solutions were added to the supporting electrolyte in order to obtain the defined palladium(II) concentrations, which ranged from $1 \cdot 10^{-7}$ to $1 \cdot 10^{-4}$ mol l⁻¹. Chloride solutions of different pH, made from 0.5 or 1.0 M KCl and 0.5 M HCl stock solutions, were chosen as supporting electrolyte, so that tetrachloropalladate [PdCl₄]²⁻ was the predominant Pd^{II} complex³⁹. The solutions were deaerated by bubbling with nitrogen. Double distilled water was used.

The chemicals used were of p.a. grade, Na₂[PdCl₄] was purchased from Bergbau- und Hüttenkombinat Freiberg (Germany), KCl and HCl from Merck and buffer solutions for pH measurements from Sensortechnik Meinsberg. Voltammograms were recorded at room temperature (22 °C) with the computer-controlled potentiostat SI 1286 (Solartron-Schlumberger, Farnborough, U.K.). For pH measurements, a glass electrode (E 56) and a pH-meter (539; both from WTW, Weilheim, Germany) were used. Any pre-treatment of the electrode (potentiostatic or at open circuit) was performed in the same solution as the voltammetric measurements.

RESULTS

Voltammetry

Cyclic voltammograms of Pd^{II} recorded at the CPE in 0.5 M chloride solution are presented in a preceding paper²⁷. Here, the CV of $4 \cdot 10^{-5}$ M Pd^{II} in chloride solution is shown, in order to give a survey of the voltammetric behaviour in the potential range from -1.2 to +1.1 V (Fig. 1). From a comparison with corresponding CV recorded in perchlorate, it is concluded qualitatively that important features of the voltammograms depend on the supporting electrolyte used. In chloride solution the appearance of peak A2, a strong current increase at $E > +0.9$ V, a shift of the cathodic current C1 to more positive potentials and simultaneous appearance of a peak C0 after preceding Pd deposition are remarkable (Fig. 1).

The characteristic anodic peak A2 at $(+0.50 \pm 0.10)$ V, which appears in presence of high palladium concentration, shows a pronounced dependence on the Pd^{II} concentration and the pre-concentration time²⁷. No oxidation peak is observed if the palladium(II) content is lower than $1 \cdot 10^{-6}$

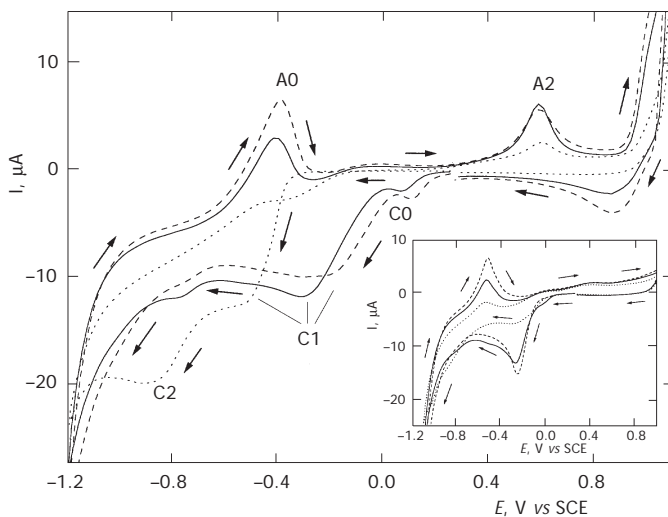


FIG. 1

Cyclic voltammograms of $2 \cdot 10^{-5}$ M Pd^{II} at CPE. Supporting electrolyte 0.5 M KCl, pH 5.0. Potential cycles from +0.25 to -1.2, +1.1 V and return. Scan rate 20 mV/s. CPE renewed before cycling. Reference electrode SCE. 1st cycle ($\cdot \cdot \cdot$), 2nd cycle (-----), 3rd cycle (- - -). Inset: Corresponding voltammograms in 0.5 M NaClO₄

mol l⁻¹. Pre-treatment at -0.3 V yields an anodic peak at +0.10 V, the peak current of which depends linearly on the Pd^{II} concentration³⁴.

As pointed out recently, two oxidation peaks (A1 and A2) are observed in $2 \cdot 10^{-5}$ and $3 \cdot 10^{-5}$ M Pd^{II} solution after potentiostatic pre-treatment³⁴. Increasing amounts of deposited Pd⁰ causes an increase in the peak current A2 and a simultaneous decrease in current A1. At higher concentration of palladium(II) or after longer pre-treatment, peak A2 increases with the treatment duration (Fig. 2, ref.³⁴). Furthermore, a pronounced reduction peak (C0) at 0 V, which increases simultaneously with A2, and a small reduction current at about +0.15 V appear.

Both oxidation peaks are also observed at Pd^{II} concentrations $\leq 1 \cdot 10^{-5}$ mol l⁻¹, when the initial potential E_i is in the range from 0 to +0.3 V and the negative reversal potential E_c between -0.3 and -0.6 V (Fig. 3). Potential reversal at more negative values causes an increase in the current A2. An increase in the palladium(II) concentration or continuation of potential sweeps results in the same change as described above.

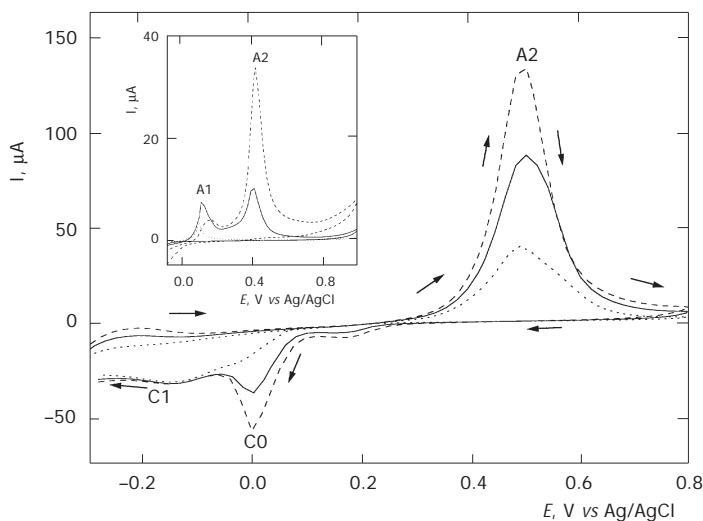


FIG. 2

Cyclic voltammograms of $1 \cdot 10^{-4}$ M Pd^{II} at CPE. Supporting electrolyte 0.5 M KCl + $1 \cdot 10^{-3}$ M HCl, pH 3.1. 0 (· · · ·), 30 (— — —) and 60 s (- - -); delay at -0.3 V (with stirring). Potential cycles from -0.3 to +0.8 V and return. Scan rate 20 mV/s. Reference electrode Ag/AgCl/KCl(sat.). *Inset*: Cyclic voltammograms of $1 \cdot 10^{-5}$ (· · · ·), $2 \cdot 10^{-5}$ (— — —) and $3 \cdot 10^{-5}$ (- - -) M Pd^{II} at CPE after pre-treatment (with stirring) at -0.1 V for 240 s. Potential cycles from -0.1 to +1.0 V and return. For other conditions see Fig. 2

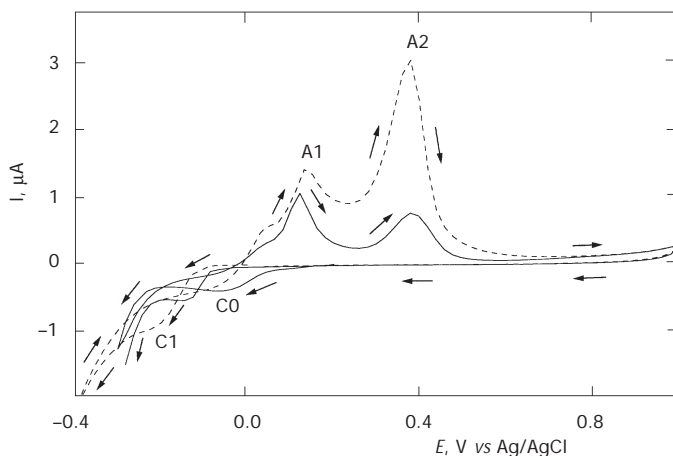


FIG. 3
Cyclic voltammograms of $6.5 \cdot 10^{-6}$ M Pd^{II} at CPE. Supporting electrolyte 0.5 M KCl, pH 5.0. Potential cycles from +0.2 to -0.3, +1.0 and -0.3 V (-----); from 0 to -0.5, +1.0 and -0.5 V (- - - -). Scan rate 20 mV/s. CPE renewed after each run. Reference electrode Ag/AgCl/KCl(sat.)

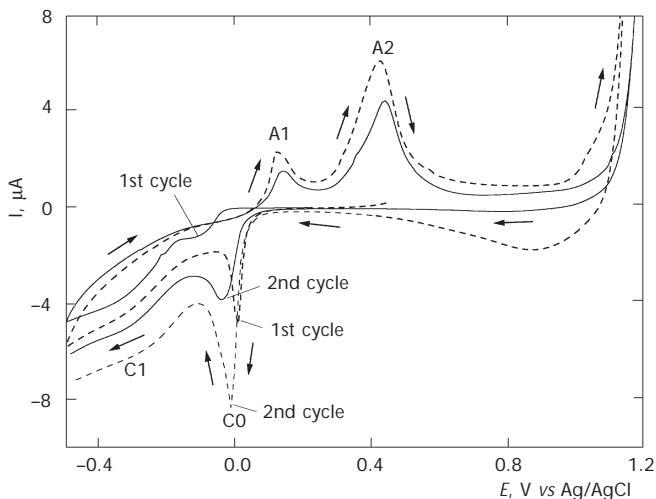


FIG. 4
Cyclic voltammograms of $2.6 \cdot 10^{-5}$ M Pd^{II} at CPE. Supporting electrolyte 0.5 M KCl, pH 5.5. Potential cycles from 0 V (vs open circuit), to -0.5, +1.2 and to -0.5 V after 45 s delay at open circuit conditions (with stirring). Scan rate 10 mV/s. 1st cycle (-----), recorded immediately after pre-treatment; 2nd cycle (- - - -) 360 s after the 1st cycle. CPE surface renewed before the pre-treatment. Reference electrode Ag/AgCl/KCl(sat.)

Pre-Concentration at Open Circuit

The oxidation peaks A1 and A2 also appeared after electrode was left at open circuit, as shown by an example in Fig. 4. Furthermore, the small reduction peak C0 (at about -0.10 V in the first negative scan) increases considerably during cycling and shifts to less negative potentials. The peak current increases and its shape changes to the pronounced, sharp peak at about 0 V with half peak width $\Delta E_{p/2} < 60$ mV. The occurrence of the narrow reduction peak C0 and its shift is presumably caused by the deposition of larger amounts of palladium at the CPE surface and its subsequent anodic treatment. Considerable anodic currents flow at $+1.2$ V, indicating an oxidation process, which is not observed in the absence of chloride (*cf.* Inset of Fig. 1).

In the presence of $1 \cdot 10^{-4}$ M Pd^{II}, peaks A2 and C0 appear during potential sweep between -0.3 and $+0.8$ V. Peak currents of both peaks increase with the number of cycles (Fig. 5). Peak current C0 increases further with additional potential cycles with the same CPE and a small anodic current A1 appears at about $+0.10$ V while the peak current A2 decreases simultaneously. The peaks C0 and A1 are presumably caused by a single redox couple. Both the formal potential E_F and the difference of the peak potentials $\Delta E = E_{p,a} - E_{p,c}$ remains constant ($E_F = +0.04$ V, $\Delta E = 0.12$ V) for C0 and A1.

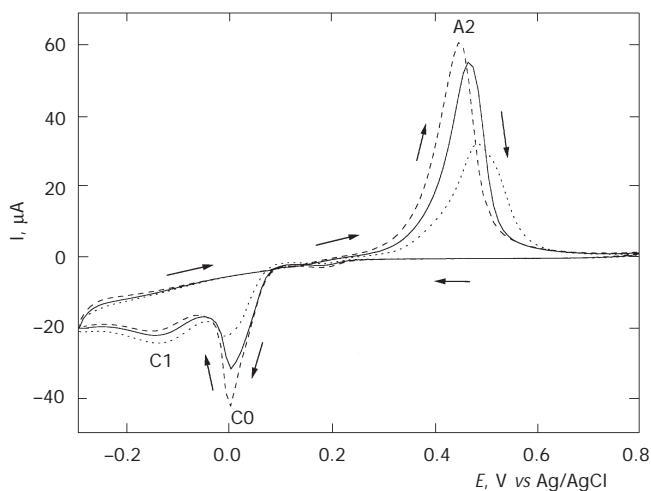


FIG. 5
Cyclic voltammograms of $1 \cdot 10^{-4}$ M Pd^{II} at CPE. Supporting electrolyte 0.5 M KCl + $1 \cdot 10^{-3}$ M HCl, pH 3.1. Three potential cycles from -0.3 to $+0.8$ V and return (without break). Scan rate 10 mV/s. CPE renewed before cycling. Reference electrode Ag/AgCl/KCl(sat.)

Voltammetric Behaviour After Anodic Treatment

In order to elucidate the influence of positive potentials after preceding palladium deposition, potentiostatic treatment at potentials $E_{AT} > +0.8$ V was performed and CV with E_{AT} as initial potential was recorded. An example obtained after holding potential for 30 s at -0.3 V with stirring and for 60 s at $+1.0$ V without stirring is shown in Fig. 6. A striking feature is the appearance of redox couple with sharp peaks at $E_{p,c} = -0.005$ V and $E_{p,a} = +0.100$ V, where the peak currents increase during application of potential cycles and the half widths decrease with the number of cycles. The peak potentials are reproducible within ± 0.005 V range in repetitive cycles. The "inverse" peak A^* is observed at $+0.80$ V in the first cycle after cathodic palladium deposition and subsequent application of positive potential (Inset of Fig. 6). Furthermore, a small anodic current is noticed between $+0.8$ and $+1.0$ V in the positive scan (Inset of Fig. 6).

The cathodic peak C0 depends on the deposited palladium amount as well as on the potentiostatic treatment of the electrode at positive poten-

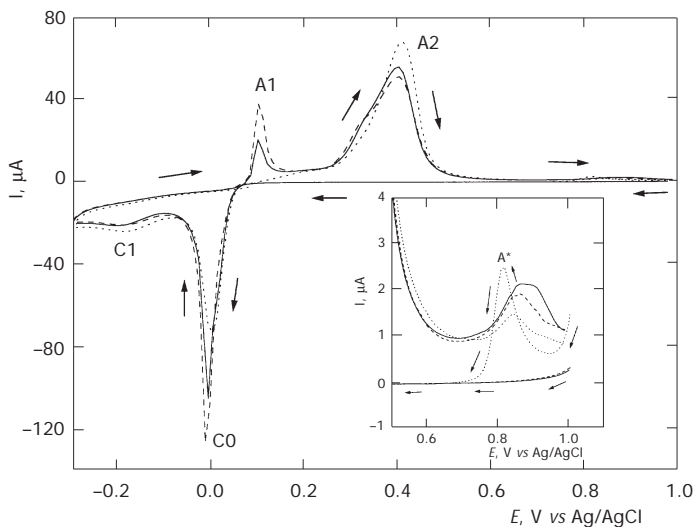


FIG. 6

Cyclic voltammograms of $1 \cdot 10^{-4}$ M Pd^{II} at CPE. Supporting electrolyte 0.5 M KCl + $1 \cdot 10^{-3}$ M HCl, pH 3.1. Potential cycles from $+1.0$ to -0.3 V and return, recorded after 30 s delay at -0.3 V (with stirring) and 60 s delay at $+1.0$ V (without stirring). Scan rate 10 mV/s. CPE surface renewed before the potentiostatic treatment. Reference electrode Ag/AgCl/KCl(sat.). *Inset*: Magnified voltammograms in the potential range from $+0.5$ to $+1.0$ V. 1st cycle (\cdots), 2nd cycle (----), 3rd cycle (- - -)

tials. Figure 7 shows dependence of the peak C0 on the duration of the negative potential treatment (after a cycle with potential reversal at +1.2 V). The peak potential shifts to less negative values when the amount of deposited palladium increases. Furthermore, a shoulder at peak C0 is noticeable (Fig. 7). After potentiostatic treatment at -0.5 V and then at $+1.2$ V two peaks are observed in the potential range between 0 and -0.2 V (not shown).

DISCUSSION

The voltammetric behaviour of palladium(II) at the CPE in chloride solution at negative potential was discussed in preceding papers^{27,40}. The potentiostatic deposition of palladium at the CPE and the existence of different surface states of Pd^0 is the subject of a communication published recently³⁴. Voltammetric behaviour of palladium(II) in chloride solution, where the tetrachloropalladate $[\text{Pd}^{\text{II}}\text{Cl}_4]^{2-}$ is the predominant palladium form, is studied after preceding deposition of Pd^0 . Points of interest are dissolution of deposited Pd^0 , the effect of anodic treatment and the surface reactions at the CPE.

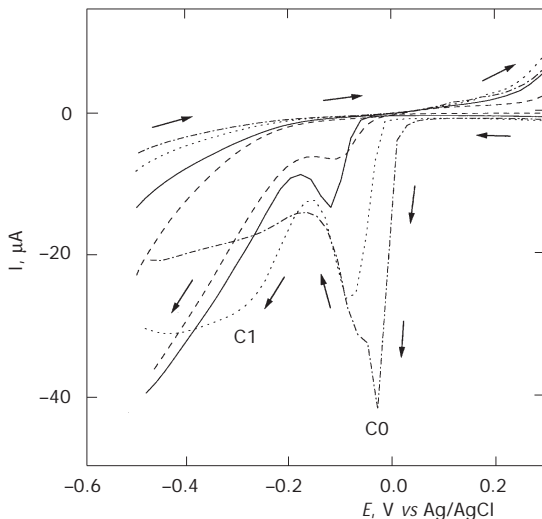


FIG. 7

Cathodic part of cyclic voltammograms of $2.6 \cdot 10^{-5}$ M Pd^{II} at CPE. Supporting electrolyte 0.5 M KCl, pH 5.5. Potential cycles from -0.5 to $+1.2$ V and return after 0 (—), 60 (---), 120 (···) and 240 s (- · - · -); delay at -0.5 V (with stirring). Scan rate 20 mV/s. Reference electrode Ag/AgCl/KCl(sat.)

Oxidation Peaks A1 and A2

From the appearance of two oxidation peaks A1 and A2 and the concentration dependence (Figs 2 and 3) it can be concluded that palladium is at first deposited as a monolayer while a multilayer is formed if larger amounts are deposited³⁴. The oxidation peak A1 at about +0.10 V indicates the dissolution of the monolayer, whereas peak A2 (at $E_p = +(0.50 \pm 0.10)$ V) represents oxidation of the palladium multilayer. Current-time plots recorded during the potentiostatic deposition of Pd⁰ confirm the interpretation. At low concentration of Pd^{II} ($c \leq 2 \cdot 10^{-5}$ mol l⁻¹) the current increases linearly with time, whereas at larger concentration the linear part is followed by a stronger current increase³⁴. The different current-time dependencies correspond to the anodic peaks A1 and A2 and the peak charges (Table 1 in ref.³⁴). Furthermore, palladium cannot be deposited at CPE at potentials more positive than A1 (ref.³⁴).

From previous experimental results²⁷ and from current study we can conclude that the dissolution of Pd⁰ at A2 is not complete and Pd⁰ remains partly on the electrode surface. As anodic current flows at potentials positive from peak A2 (Figs 2 and 4) the continuation of slow dissolution of deposited Pd⁰ is assumed. Also, there are indications that positive potentials applied on the CPE do not lead to complete dissolution of the palladium(0) (see below).

As we have found, two palladium oxidation peaks appear at the CPE not only after potentiostatic treatment³⁴, but also after period of open circuit conditions (Fig. 4) as well as after a preceding sweep to negative potentials (Fig. 3). In presence of $1 \cdot 10^{-4}$ M Pd^{II}, only peak A2 at more positive potentials is observed (Fig. 5). When additional cycles are recorded (after preceding deposition of Pd⁰) peak A1 appears accompanied by a simultaneous increase of C0 and by the change of its shape. Therefore, the question arises whether a Pd⁰ monolayer can be formed under these circumstances or another reason exists for the appearance of peak A1.

Cathodic Peaks C0 and C1

The reduction peak C1 is attributed to the reduction of palladium(II) species from the solution and to the deposition of Pd⁰ on the electrode surface^{27,40}. The peak potential shifts to the positive direction with number of potential cycles due to the Pd⁰ deposition in preceding cycles. Increasing Pd^{II} concentrations causes also the potential shift and the increase in the C1 peak current, as shown in preceding papers^{27,40}. Peak C1 represents the

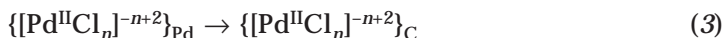
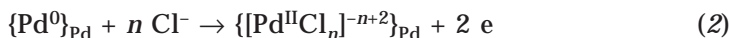
reduction of $[\text{Pd}^{\text{II}}\text{Cl}_4]^{2-}$ (Eq. (1)) in accordance with the experimental data. Its positive shift points to an influence of the deposited Pd^0 on reaction (1). The reaction (1) seems to take place on the deposited palladium (instead of the carbon surface), causing decrease of the Pd deposition overvoltage and the observed shift of C1.



An additional reduction current at about +0.1 V in subsequent cycles was already mentioned⁴⁰. The striking feature of the study is the presence of the pronounced reduction peak C0 at about 0 V (*cf.* Figs 2, 4–7), which appears after deposition of large amounts of Pd^0 and potential sweeps to $E > +0.8$ V (Figs 2, 4, and 7) or after application of corresponding potentials (Fig. 6). In Figs 3 and 7, it is demonstrated that the peak current and peak shape depend on the amount of Pd^0 deposited. Particularly sharp peak C0 (with half widths ≤ 45 mV) and peak current up to 100 μA appears after the potentiostatic treatment at +1.0 V after preceding palladium deposition (Fig. 6).

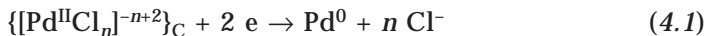
Furthermore, the oxidation peak A1 is observed in the positive potential sweep at about +0.1 V, when the C0 peak appears in the preceding negative scan (Fig. 6). The peak A1 also appears when additional cycles with +0.8 V as positive potential proceeded after palladium deposition and a rest time.

The peaks C0 and A1 appear after the deposition of large amounts of palladium, dissolution of Pd^0 (in the potential range of A2) and the subsequent application of positive potential. Similar results can be obtained after cathodic deposition, a potential jump to $E > +0.8$ V and a delay at this potential. During the positive scan or potential holding at $E > E_p(\text{A2})$, a slow dissolution of the Pd^0 occurs under participation of chloride ions of the supporting electrolyte. For Pd as well as for other noble metals, the formation of adsorbed or chemisorbed tetrahalide complexes is the initial step of the dissolution, followed by the desorption^{22,25}. The oxidation peak A2 is not observed in sulfates or perchlorates⁴¹. Therefore, it is assumed that chlorides are involved in the dissolution of Pd^0 (Eq. (2)). In the potential range of A2, the palladium multilayer is oxidised, forming chloropalladate(II) species (probably $[\text{Pd}^{\text{II}}\text{Cl}_4]^{2-}$ complex) adsorbed or chemisorbed on the remaining palladium(0). When large amounts of Pd^0 are oxidised and the surface concentration of chloropalladate increases, then chloropalladate either forms multilayers on Pd or it diffuses from palladium islands into the solution or to the uncovered carbon (Eq. (3)).



The subscripts Pd and C (at the braces) indicate the corresponding species localised at palladium islands or at the uncovered carbon.

Application of positive potentials on carbon electrodes causes an increase in concentration of carbon surface oxidic groups⁴². On the other hand, chemisorption of chlorides and formation of carbon–chloride bonds at the electrode surface, known from glassy carbon^{35,36}, is also probable. As peaks C0 and A1 appear after anodic treatment of CPE which involves chlorination of the carbon surface, it is assumed that the chloropalladate ions (formed during the Pd⁰ dissolution and then sorbed at the palladium islands) move to the “chlorinated” carbon regions by surface diffusion. The surface-bounded chloride facilitates the diffusion. The reduction of surface-bounded chloropalladate on carbon regions of the electrode surface gives rise to the cathodic current C0 (Eq. (4)).



or



It can be concluded that peaks C0 and A1 represent single redox couple (Inset of Fig. 5, Fig. 6), although A1 is not observed in each case (Figs 3 and 5). In particular, sharp redox peaks (Fig. 6) and constant difference of peak potentials points to an immobilised palladium species, probably Pd^{II} and Pd⁰. The difference $\Delta E_p = E_{p,c} - E_{p,a}$ is (0.11 ± 0.01) mV. For immobilised redox systems ΔE_p is near 0 V at metal and solid carbon electrodes⁴³. But in the case of carbon paste electrodes with heterogeneous electrode surface, $\Delta E_p > 0$ V is expected and observed, even in the case of reversible redox systems^{44,45}.

Because of the appearance of peak A1 after treatment at positive potential (Fig. 6), the formation of a chloropalladate(0) complex at the electrode surface is concluded according to Eq. (4.2). Peak A1 appears when the Pd⁰ monolayer at CPE is oxidised³⁴. Therefore, it is probable that the chloro-

palladate complexes are localised on the carbon region of the electrode, not on Pd^0 islands. The peak A1 is in every case smaller than C0, because the formed chloropalladate(0) complex is either partly decomposed or it is not re-oxidised completely.

The reason for the occurrence of the peak shoulder at C0 (Fig. 7d) or of two cathodic peaks in the potential range of C0 (see above) could not be elucidated. This behaviour, however, can be caused by the existence of the phase boundary between palladium islands and the carbon, since the reduction according to Eq. (4) presumably occurs at different potentials, when the charge transfer takes place at the carbon or the palladium carbon interface.

*Reactions at Positive Potentials and the "Inverse" Peak A**

At potentials more positive than peak A2 a small anodic current flows (Figs 2 and 4) apparently due to continuation of the slow dissolution of the deposited Pd^0 . The strong rise in the anodic current at $E \geq + 0.9$ V shows onset of a further oxidation process. The oxidation current depends on the chloride concentration as well as on the amount of deposited Pd^0 (Figs 1 and 4). Therefore, the oxidation of the carbon surface under participation of chloride^{35,36} and tetrachloropalladate³⁷ is assumed. The influence of the palladium on carbon oxidation and chlorination is attributed to chloropalladate(II) adsorbed on the carbon, facilitating thus the oxidation of carbon surface and chloride transfer.

The "inverse" peak A* is observed only during the first potential sweep after positive potentials were applied on the palladium deposited CPE. Therefore, it is assumed that the peak current A* is caused by the continuation of a slow surface reaction taking place at positive potentials. As the "inverse" peak is not observed in absence of Pd^{II} , the participation of $[\text{Pd}^{\text{II}}\text{Cl}_4]^{2-}$ (as the prevailing palladium species) or other chloropalladate species in the electrode surface reaction can be expected. The slow rearrangement of sorbed chloropalladate species in the carbon regions (e.g. the formation of ordered chloropalladate structures perpendicular to the surface), the oxidation of Pd^{II} to higher oxidation states or the reaction of the palladium(II) with coordinating carbon surface groups can be reasons for observed behaviour. The study of this phenomenon is still under way.

CONCLUSIONS

The appearance of two palladium oxidation peaks in dependence on the deposited amount of Pd⁰ reported recently³⁴ was studied by voltammetry. The existence of different surface states of palladium(0) at carbon paste electrodes, possibly formed by monolayer and multilayer depositions³⁴, was confirmed by presented results. This finding indicates the formation of metal monolayers on the heterogeneous CPE surface.

After deposition of Pd⁰ and anodic treatment, a reduction current (C0) is observed at about 0 V in the following negative potential sweep. Its peak current increases with the amount of Pd⁰ deposited. Peak C0 is well pronounced and narrow after potential cycling to $E > +0.8$ V or after potentiostatic treatment at corresponding potentials; it increases during potential cycling in the range from $-(0.4 \pm 0.1)$ to $+0.9$ or $+1.2$ V.

The application of positive potentials leads also to the appearance of small, but pronounced peak A1 (with E_p at about $+0.10$ V) in the following potential cycle. The peaks C0 and A1 appear to be attributed to single redox peak of chloropalladate complex formed due to the dissolution of larger amounts of Pd⁰ during the anodic treatment. Since this process (according to experimental results obtained with glassy carbon) is known to be associated with the chemisorption of chlorides and the formation of carbon-chlorine bonds, the formation of $[\text{Pd}^{\text{II}}\text{Cl}_n]$ complexes at the carbon surface is possible. The chloropalladate complex $[\text{Pd}^{\text{II}}\text{Cl}_n]$ is reduced at potential of C0, probably to the corresponding palladium(0) complex, which is then re-oxidised at potential of A1. The suggested mechanisms of the electrode reactions, although rather speculative, enable interpretation of the experimental results.

The palladium surface complex formed at positive potentials appears to be stable during potential cycling, thus the existence of defined palladium-chloride structures at the carbon can be expected. Therefore, the formation of the chloropalladate surface complex represents an example of the formation of stable transition-metal chloro complexes at carbon surfaces. Preceding metal deposition and the following anodic treatment in chloride solution could be a suitable procedure for the modification of carbon electrodes with metal chloro complexes.

This paper represents a further example of oxidative formation of a transition-metal surface complex at the CPE. Similar mechanism was found recently for the formation of surface complexes of silver(I) and palladium(II) at CPE modified with organic ligands^{31,38}.

SYMBOLS

A0, A1, A2	anodic peaks
A*	"inverse" peak, <i>i.e.</i> , anodic peak in the cathodic sweep
C0, C1, C2	cathodic peaks
CPE	carbon paste electrode
CV	cyclic voltammetry
E	electrode potential
E_{AT}	potential of the anodic treatment
E_c	negative reversal potential
E_i	initial potential
E_F	formal potential $E_F = 1/2 (E_{p,a} + E_{p,c})$
E_p	peak potential
$E_{p,a}$, $E_{p,c}$	peak potential of the anodic and the cathodic peak, respectively
ΔE_p	difference of the peak potentials $\Delta E_p = E_{p,a} - E_{p,c}$
$\Delta E_{p/2}$	half width of the peak, <i>i.e.</i> , peak width at $i = i_p/2$
i	current
i_p	peak current
SCE	saturated calomel electrode Hg/Hg ₂ Cl ₂ /KCl(sat.)

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