

ELECTROLYTIC COATINGS (LAYERS) DEPOSITED FROM PALLADIUM(II) SALTS

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Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.

In contrast to a number of investigations concerning preparation of layers and coatings of palladium(II) oxides this communication describes a reproducible electrolytic preparation from activation baths containing Pd(II) ions of coatings with hydrated palladium oxides, in particular on platinum supports. The voltammetric curves of coatings formed in such a way are reproducible over the whole pH range and exhibit an irreversible cathodic-anodic couple of peaks. For the voltammetric curve on an active layer deposited on a platinum support from a solution of Pd(NO₃)₂ at pH 7.03 E_p^k is +0.02 V and E_p^a +0.33 V (vs SCE). The observed character of the pH dependences for the peak potentials and current densities with a similar, mostly linear, behaviour has been also observed with layers deposited on glassy carbon or nickel. The deposited layers containing hydrated palladium oxides exhibit oxidative activity as follows from voltammograms in slightly acidic to neutral and strongly alkaline region. These curves point to the ability to oxidize not only ethanol but also toluene used as a with difficulty oxidizable model substrate.

The ecological motivation with strict economics led in the eighties to a violent expansion of indirect organic electrosynthesis in which ingenious electrochemically regenerable redox systems¹ play an important role.

One type of indirect organic electrosynthesis is based on deposition of an active redox catalyst – mediator – on the surface of a suitable support electrode. The reaction proper, i.e. the transformation of the educt, and the regeneration of the mediator take place in a single cell during electrolysis. A classical example of this electrosynthetic method is the industrial electrolytic variant of the fundamental oxidative step in the vitamin C production as developed by Robertson and Seiler². Its main step is the deposition of NiO(OH) (ref.³) on a nickel electrode and the use of this layer for the oxidation of the hydroxymethyl group of the intermediate to a carboxylic group in an aqueous solution of NaOH. In further investigations the conditions for the application of electrochemically deposited NiO(OH) not only to the electrooxidation of alcohols to carboxylic acids but also of primary amines to nitriles⁴ were studied.

The search for suitable mediators deposited on the electrode and functioning in a similar way in situ in the cell is very attractive and prospective.

All this led to performing the present investigation which follows the possibilities of preparation, the properties and the use of hydrated palladium(IV) oxide coatings in indirect organic electrosynthesis.

The earlier literature⁵ describes a preparation of hydrated palladium oxide, $\text{PdO}\cdot x\text{H}_2\text{O}$, by precipitating palladium salts (chloride or nitrate) by an aqueous solution of Na_2CO_3 or NaOH . Further, there is also an electrolytic formation of $\text{Pd}_2\text{O}_3\cdot x\text{H}_2\text{O}$ from $\text{Pd}(\text{NO}_3)_2$ solutions in 2 mol l^{-1} HNO_3 at -8°C at a platinum anode and a current density 0.5 A cm^{-2} . In a divided cell and at similar conditions with $j = 1.6\text{ A cm}^{-2}$ the hydrate $\text{PdO}_2\cdot x\text{H}_2\text{O}$ can be prepared. The research of layers and coatings of palladium oxide culminated in the fuel cell investigation; the electrode materials for stable anodes⁶ of the DSA type are still being developed for brine and melts electrolysis. Not unimportant are also the investigations of the system Pd/PdO_x in corrosion science⁷.

In this paper, however, the studied layers were chiefly prepared on platinum and nickel supports by electrolytic deposition from palladium(II) ions solutions.

EXPERIMENTAL

Both for depositing coatings and for voltammetric measurements platinum wire electrodes were used with o.d. 0.5 mm and a surface area of 9.4 mm^2 . The nickel wire electrodes had o.d. equal to 0.6 mm and a surface of 12.2 mm^2 , the glassy carbon stick electrodes had o.d. equal to 3 mm and a surface of 18.8 mm^2 . Before a new covering the old coating was removed in aqua regia at laboratory temperature, the electrodes were then rinsed by concentrated hydrochloric acid and finally washed thoroughly by distilled water. During deposition of the coating they functioned as working electrodes, the auxiliary electrode was a platinum wire. Both in forming the layer and in voltammetry of the deposited layers a saturated calomel electrode (SCE) was used as a reference electrode. The composition of the activation baths used in deposition is shown in Table I. During the deposition of coatings containing hydrated palladium oxides the electrode was polarized in 4–6 cycles lasting 15 to 20 seconds by a current whose polarity was changed in each cycle. The current density was $2\text{--}200\text{ mA cm}^{-2}$.

For investigating the pH-dependence of the voltammetric curves of the surface layers a freshly deposited new layer was used for each new pH-value. The dependences of peak currents — expressed in current densities, j_p/pH — were obtained always with the use of a single coating. Palladium(II) salts were prepared from metallic palladium by preparative procedures described by the literature⁵.

Voltammetric curves were recorded with an LP9 polarograph in connection with an x, y recorder XY 4103 at laboratory temperature and at a scan rate 10 mV s^{-1} . Britton–Robinson buffers prepared from analytic grade reagents were made use of. The buffer solutions in voltammetric measurements were degassed by a stream of nitrogen. The pH values of the solutions were measured with an electronic pH meter Radelkis OP211-1 with a glass electrode.

Preparative electrolyses serving to the examination of oxidative activity of the layers were performed in divided glass cells on *o*-toluenesulfonamide making use of the procedure and the equipment described in our preceding paper⁸. The active layers of hydrated Pd(IV) oxides

were deposited from the mentioned baths (cf. Table I) by applying similar current densities and techniques as in the study of layers by voltammetry.

RESULTS

A platinum wire electrode was (in voltammetric recordings) alternately, negatively and positively polarized in an activating solution with palladium(II) acetate (Table I). The current density was about $2-5 \text{ mA cm}^{-2}$. A grey-black coating was formed on the electrode surface during the polarization. The cyclic voltammograms showed an increase both of the cathodic and the anodic peaks with the number of cycles as follows from Fig. 1. The formation of a stable consistent black coating, however, requires a considerably higher current density ($150-200 \text{ mA cm}^{-2}$) at alternating polarization. Then, according to the given polarization program (Fig. 2), an active coating formed within a short time on the platinum electrode; this coating is suitable for voltammetric investigations. The active layers were also deposited from activation solutions prepared from palladium(II) nitrate and filled up with sodium sulfate or nitrate (Table I). In particular, coatings prepared from activation baths containing Pd(II) nitrate exhibited a better stability and oxidative activity (cf. Fig. 2). For the cathodic peak E_p^k is $+0.02 \text{ V}$, for the anodic one E_p^a is $+0.33 \text{ V}$ (vs SCE) in an activation bath pH 7.03.

The active layers yielding peaks of almost equal height in cyclic voltammograms were deposited on platinum wire electrodes even from acid solutions containing

TABLE I
Applied activation baths

Bath	Composition	pH
Acetate	1.4 g (6.5 mmol) $(\text{CH}_3\text{COO})_2\text{Pd}$ 4.0 g (48.7 mmol) CH_3COONa 20 ml distilled water	10.5
Trifluoroacetate	0.5 g (1.5 mmol) $(\text{CF}_3\text{COO})_2\text{Pd}$ 2.7 g (20 mmol) CF_3COONa 20 ml distilled water	1.40
Sulfate	0.4 g (2 mmol) PdSO_4 1 g (7 mmol) Na_2SO_4 anhydrous 20 ml 0.4M Britton-Robinson buffer	6.80
Nitrate	0.5 g (2.1 mmol) $\text{Pd}(\text{NO}_3)_2$ 1.7 g (20 mmol) NaNO_3 20 ml 0.4M Britton-Robinson buffer	6.80

palladium(II) trifluoroacetate. Voltammograms of deposited coatings in Britton–Robinson buffers showed a single cathodic and usually one anodic peak. When following the pH-dependences the clean platinum wire electrode was always freshly covered by the active layer for each pH-value. Moreover, the first recordings after the deposition – if the last cycle was the anodic polarization – showed a diffusion-controlled cathodic peak which disappeared on repeating the recordings in acid and neutral region. The dependence of E_p on pH of coatings deposited from palladium acetate solutions on platinum both for cathodic and anodic peaks of the voltammogram is shown in Fig. 3. The cathodic peak potential E_p^k is a linear function of pH virtually over the whole region with a slope for E_p^k equal to $-75 \text{ mV} \cdot \text{pH}^{-1}$. The anodic peak is badly developed in the alkaline region where, moreover, a discontinuity could be observed on the $E_p^a = f(\text{pH})$ plot. In addition to this, the formation of a stable cathodic prepeak (probably diffusion-controlled) was observed and also the appearance of a small more negative anodic peak. The voltammetric curves of layers deposited on platinum support from solutions containing Pd(II) nitrate are very similar to those obtained with coatings from sulfate baths. Their linear dependence of E_p on pH is $-65 \text{ mV} \cdot \text{pH}^{-1}$ for E_p^k and $-70 \text{ mV} \cdot \text{pH}^{-1}$ for E_p^a .

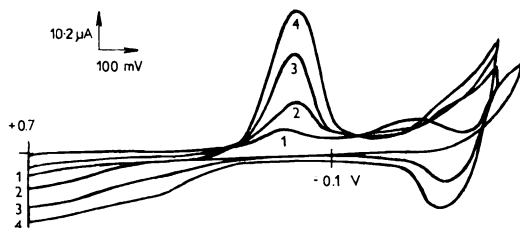


FIG. 1

Voltammograms on a platinum electrode in 1M- CH_3COONa with 0.4 mM-Pd. $\cdot(\text{CH}_3\text{COO})_2$, recorded in the sequence 1, 2, 3, 4; scan rate 10 mV s^{-1} , SCE

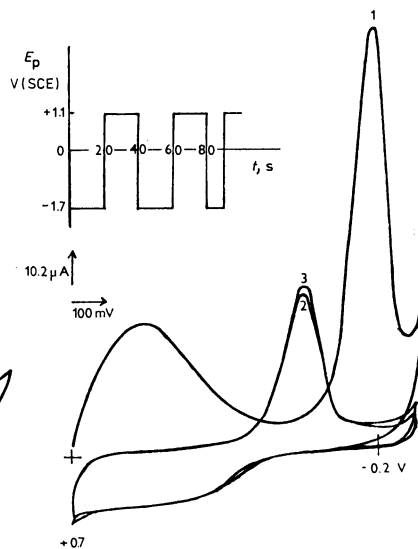


FIG. 2

Voltammograms of the active coating deposited on a Pt support from a $\text{Pd}(\text{NO}_3)_2$ bath; recorded in the same solution pH 7.02; 1,2,3-sequence of recordings after the activation according to the program

The dependence of peak potentials in voltammetric curves recorded with coatings from solutions containing $(\text{CF}_3\text{COO})_2\text{Pd}$ is more similar to that obtained with coatings deposited from an acetate solution. The values of cathodic peak potentials of coatings from the trifluoroacetate bath are somewhat more positive than those with coatings deposited from acetate solutions. The slope of the linear plot E_p^k vs pH is $-70 \text{ mV} \cdot \text{pH}^{-1}$ for coatings from trifluoroacetate baths, the anodic peaks do not appear again in alkaline solutions. Figure 4 demonstrates an example of $j_p = f(\text{pH})$ both for cathodic and anodic peaks. The dependence was measured for a coating deposited on platinum from a trifluoroacetic bath. All voltammetric curves for the dependence $j_p = f(\text{pH})$ were recorded on a single deposited coating. The highest anodic peaks result in strongly acidic media and exhibit a monotonous decrease in height in the direction towards the neutral region. In the slightly alkaline region are the anodic peaks not developed. The height of cathodic peaks only slightly varies towards the neutral region; at $\text{pH} < 7$ it abruptly decreases with a minimum between $\text{pH} 9$ and 10 . This minimum is followed again by a sudden increase in the height of cathodic peaks towards strongly alkaline solutions. This overall shape of the $j_p = f(\text{pH})$ curve is characteristic and similar also for coatings deposited from the other activation solutions reported in this communication. When studying the deposited layers containing hydrated palladium oxides we also studied the possible influence of the

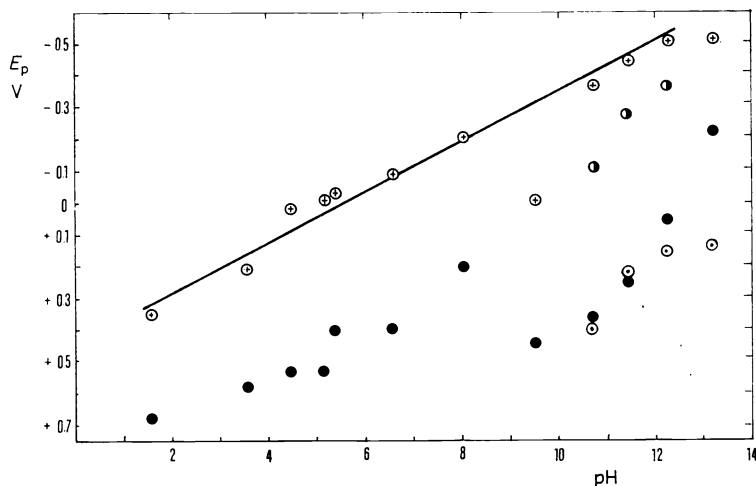


FIG. 3

Dependence of peak potentials E_p on pH at a platinum electrode with an active surface generated from an acetate bath; the electrode with the coating was transferred into the solution with the corresponding pH; \oplus cathodic peak; \odot cathodic more positive prepeak; \bullet anodic peak; \otimes anodic more negative peak

electrode support on the properties of active coatings. In addition to the fundamental investigations carried out with a platinum wire electrode we also studied the coatings deposited on glassy carbon and nickel. The dependence of E_p on pH for layers deposited from Pd(II) solutions on a glassy carbon electrode is linear with a slope equal to $-75 \text{ mV} \cdot \text{pH}^{-1}$ for cathodic and anodic peaks. The plot j_p vs $f(\text{pH})$ exhibits a typical decrease for cathodic peaks in the slightly alkaline region with a minimum at pH 8 and a new increase in strongly alkaline solutions.

When coating nickel wire electrodes from a bath with trifluoroacetate a black layer resulted which gave voltammetric curves the character of which corresponds to layers from acetate baths deposited on platinum. The linear plot of E_p^k vs pH had a slope equal to $-65 \text{ mV} \cdot \text{pH}^{-1}$ whereas the anodic peaks are missing in the alkaline region pH 7–12. Only at the extremely alkaline value pH 13–20 an anodic peak developed. In acidic and neutral media well developed anodic peaks are also linearly dependent on pH with a slope equal to $-80 \text{ mV} \cdot \text{pH}^{-1}$. The dependence $j_p = f(\text{pH})$ for the same layer on a nickel support has a monotonous decrease in the height of cathodic peaks with a minimum at pH 10. For higher pH values the straight line suddenly increases so that the highest value is obtained at pH 13–20.

Cathodic and anodic peak potentials in voltammetric curves for coatings deposited on platinum supports are on average separated by 320 to 350 mV with minimum values near to 270–290 mV in strongly acidic and alkaline solutions. In Table II the results of preparative electrolytic oxidations are summarized on palladium oxide coatings prepared as described above. For the first tests of oxidative activity of the surface layers *o*-toluenesulfonamide was used whose oxidation had been described in a preceding paper⁸. The current efficiency was not evaluated since the consumed charge was clearly bigger as a result of a parallel oxygen development on the working electrode: the parasitic reaction could not be fully suppressed.

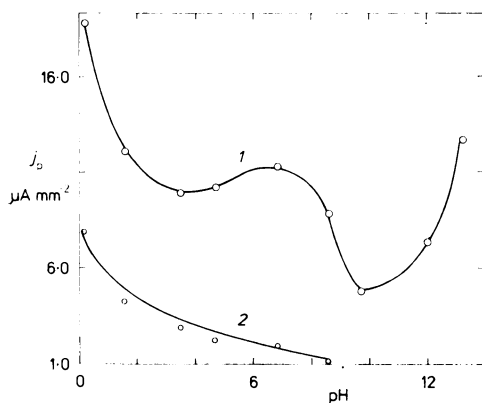


FIG. 4
Dependence j_p vs pH for the active coating deposited from a $(\text{CF}_3\text{COO})_2\text{Pd}$ bath onto a platinum support; 1 cathodic peak; 2 anodic peak

DISCUSSION

The detailed study of voltammetric curves of active layers revealed that for obtaining a cathodic peak in the neutral up to alkaline region one must start the recording from positive potentials +0.8 up to +0.5 V. When starting the recording from a potential near the foot of the expected cathodic peak, i.e. from less positive potentials, this peak does not appear or is only small. It does not suffice that in the immediately preceding cycle and in the same solution the layer was polarized to sufficiently positive values in the formation of the anodic peak. This finding points to a rapid decomposition of the active oxidized form in the layer formed by anodic polarization. In acid media the stability of the oxidized form in the coating is higher and enables the formation of the cathodic peak even at more negative starting potential of the recording, lying on the foot of the expected cathodic peak. From this fact the justification of anodic polarization follows when forming active layers of hydrated palladium oxide. This also points to a more complicated reaction mechanism of the irreversible redox transformation in the active layer.

The course of depositing the active layer on electrodes and the voltammetric curves of the layers confirms the existence of a covalent bond of oxygen in the coating but does not exclude even the possibility of a partial and temporary adsorption bonding of oxygen in the structure of the coating. When depositing layer from active solutions of palladium salts which takes place more in a galvanostatic mode, the current density is 50–200 mA cm⁻². At polarization potentials +1.1 V and -1.7 V (vs SCE)

TABLE II

Parameters of model oxidative reaction *o*-TSA → saccharine + 6e in the presence of NaOH

Reaction conditions	Undivided cell single batch	Flow-through cell
Electrolyte	0.5% NaOH 0.5% <i>o</i> -TSA	0.5% K ₂ CO ₃ 0.5% <i>o</i> -TSA
Electrodes	anode Ni/hydrated Pd-oxides cathode Ni	Pt/hydrated Pd-oxides Pt
Temperature	59–61°C	57–58°C
Current density	12 mA cm ⁻²	15 mA cm ⁻²
Potential (SCE)	+1.8 V	+2.8–+3.0 V
Material yield	50% saccharine 20% <i>o</i> -TSA loss by oxidation	55% saccharine 25% <i>o</i> -TSA loss by oxidation

in the anodic and cathodic polarization respectively, oxygen or hydrogen are deposited in the given system. Hydrogen evolution can be observed. It is probable that the more positive diffusion-controlled cathodic peak which can be followed at pH 1.0 to 8.5 only during the first voltammetric cycle corresponds to the reduction of oxygen from the preceding anodic activation cycle. In further recordings the voltammetric curves of the same layer are already stabilized as regards their shapes, proportions and positions. It has been demonstrated that active layers containing hydrated palladium oxides may be deposited both from alkaline, neutral and weakly acidic solutions of Pd^{2+} . At the same time the voltammetric behaviour of active coatings only slightly differs. A detailed study of the formation of the active layer showed that the cathodic polarization of the electrode in an activation solution at -1.6 V (vs SCE) and $j = 100\text{ mA cm}^{-2}$ a black coating is formed whose voltammetric

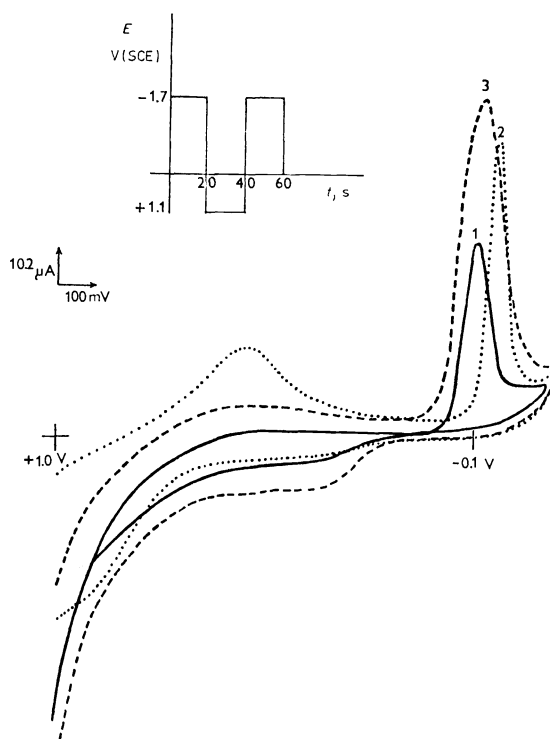
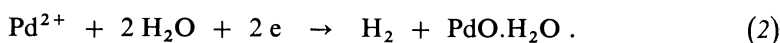


FIG. 5

Voltammetric curves of the active coating deposited on a platinum support from a $\text{Pd}(\text{NO}_3)_2$ bath at pH 6.9; recorded in the same bath; 1 after a cathodic generating polarization; 2 after an anodic generating polarization; 3 after a further cathodic generating polarization; scan rate 10 mV s^{-1} ; SCE

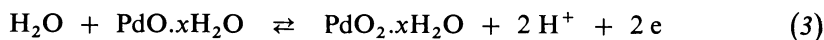
record yields a lower cathodic peak and an anodic one resembling by its position the peaks on voltammetric curves of the studied active layers (Fig. 5). In the subsequent anodic polarization of this coating at the usual potential +1.0 V and a current density of 100 mA cm^{-2} in an activation bath a cathodic diffusion-controlled, more positive peak appeared and the both existing cathodic and anodic peaks were increased. Further alternating polarization cycles caused then a mild increase in the peak height in the voltammetric curves and a stabilization of their position on the potential axis.

It is evident that in the cathodic cycle a palladium deposition occurs from an activation bath containing only $\text{Pd}(\text{CH}_3\text{COO})_2$. Simultaneously the conditions are also suitable for the formation of palladium(II) oxide hydrates, $\text{PdO}\cdot x\text{H}_2\text{O}$:



It is known that palladium salts, in particular those of weaker acids, e.g. of CH_3COOH , considerably incline to forming hydrolytic products. It has been reported⁵ that these hydrolytic products are based on various forms of $\text{PdO}\cdot x\text{H}_2\text{O}$.

Among the Pd(II) salts studied in this paper just Pd(II)-trifluoroacetate, giving an aqueous solution pH 1.9, was extremely sensitive towards hydrolysis. Even a slight increase of pH led to a deposition of brown oxides. The required pH-change may be even required in the electrode double layer, in particular during the cathodic discharge of sodium ions present in the solution. In the anodic polarizing cycle in an activation bath the oxidation of deposited palladium proceeds but also that of lower hydrated Pd oxides:



The anions A^- of the palladium(II) salt may – if necessary – recombine with protons set free during the oxygen evolution which is bonded in the palladium oxide having a higher valency.

The influence of the electrode support on the voltammetric behaviour of deposited coatings did not play any significant role at a sufficient thickness of the layer with indifferent materials (Pt, GC). In the case of layers deposited on nickel no anodic peaks appeared in the voltammogram in the alkaline region. One may expect that underneath the active palladium layer $\text{NiO}(\text{OH})$ will be formed on nickel supports in alkaline media. The differing values of anodic peak potentials in strongly alkaline solutions pH 13.2 (1% NaOH) in comparison with coatings on indifferent supports can be evidently ascribed to an interaction between palladium oxide and $\text{NiO}(\text{OH})$ layers. When applying a large-area nickel electrode with a deposited active layer

a disintegration of the nickel support proceeds during electrolysis at a higher current density. By interaction with the active palladium layer it was changed to NiO(OH).

From the difference between anodic and cathodic peak potentials in voltammograms of active coatings a distinctly irreversible behaviour follows.

Up to a temperature of 80°C the active coatings between pH 1.5 and 13 seem to be stable. They slowly dissolve in diluted solutions of mineral acids at laboratory temperature. Voltammograms of active layers containing palladium oxides and NiO(OH) deposited for comparison on platinum supports essentially differ. NiO(OH) yields a reversible couple of peaks at +0.26/+0.35 V but only in strongly alkaline media.

We also studied the oxidative activity of deposited layers containing hydrated Pd oxides. This property represents the most important aspect of the oxides and was the reason of our investigation. The anodic peak of the voltammogram of such a layer does not change by an addition of ethanol in strongly acidic media. With

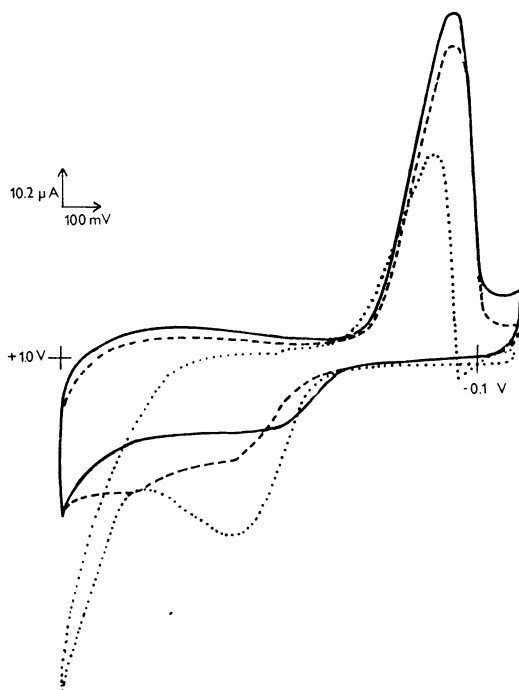


FIG. 6

Voltammetric curves of an active coating deposited from a $\text{Pd}(\text{NO}_3)_2$ bath on a platinum support; full line: Britton-Robinson buffer pH 4.7; dashed line: same buffer with toluene added; dotted line: same buffer with ethanol added; scan rate 10 mV s^{-1} ; SCE

increasing pH-values up to pH 7 an addition of ethanol causes a still more pronounced increase of the anodic peak. In strongly alkaline solutions an addition of ethanol causes an abrupt change in the shape of the curve. In a similar manner an addition of toluene and picoline also causes an increase of the anodic peak (cf. Fig. 6) in slightly acidic and neutral media as well as at pH > 12. These experiments point to the oxidative activity of the coatings; a more detailed investigation of this property is in progress. Preparative tests of the oxidative activity of the active PdO-coatings (cf. Table II) proved that for our model educt, *o*-toluenesulfonamide, studied already in our preceding papers⁸ the achieved saccharine yield is not considerably better as compared to the oxidation with the help of NiO(OH). Moreover, it can be only achieved on account of oxidative losses.

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