ELECTROCHEMICAL PROPERTIES OF ELECTRODE COATINGS CONTAINING HIGHLY OXIDATIVELY ACTIVE PLATINUM OXIDES

Jaromír HLAVATÝ and Jiří VOLKE

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 182 23 Prague 8

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By time-programmed anodic and cathodic polarization (galvanostatic conditions and undivided cell) chemically stable coatings of hydrated higher valency platinum oxides were deposited from a 10% aqueous solution of alkali hydroxide saturated with PtO_2 on platinum, nickel, titanium, iron and glassy-carbon electrode supports. Their voltammograms yield anodic and cathodic peaks over the whole pH region (0·15 to 13·20). The peaks corresponding to the transformation of higher valency platinum oxides are developed at more positive values (cathodic peaks between +0·57 and −0·35 V, and anodic peaks from +0·88 to −0·23 V vs SCE). The peaks corresponding to the transformations of PtO_2 are located in a more negative region. Upon adding toluene or its derivatives their electrocatalytic oxidation over the whole pH region is intensified by increasing the temperature to 80°C. The preparative coatings of hydrated platinum oxides prepared by the same technique on platinum grids were only deposited on a part of the electrode surface. The preparative electrolytic oxidation of toluene on these coatings leads only to low material yields: in 0·5M H_2SO_4 it gives 4% benzaldehyde and in 0·25M NaOH even less, i.e. 3%. The linear dependence of the increase of peak currents in voltammograms of coatings plotted as a function of the cathodic polarization potential (applied in the preceding preparation in strongly acidic media) points to a liberation of alkali metal cations intercalated in the coating of hydrated higher valency platinum oxides during their deposition.

In our search for electrode coatings – analogous to the system NiO(OH) – which would make possible an indirect electrocatalytic oxidation e.g. of toluene derivatives[1] (i.e. with the exclusion of an ionic redox system) we first investigated the properties of palladium oxide coatings[2] but later we turned our attention to platinum oxides. Hydrated platinum oxides should posses both better chemical resistivity and electrocatalytic properties. However, there are only few data concerning the properties of appropriate oxides to be found in recent literature. There is a larger number of papers investigating the platinum oxides prepared by different techniques of anodic polarization of platinum supports in sulfuric acid solutions[3–5]. These frequently repeated procedures aiming to generate higher platinum oxides result always in $Pt(OH)_4$ or PtO_2 according to XPS analysis. In Gmelin's compendium[6] a great number of details were found concerning particularly platinum(II) and platinum(IV) oxides. Wöhler[7] describes a preparation of PtO_3 by electrolytic oxida-

tion of a PtO_2 solution in 2M KOH. None of authors[3-5] presented above tried to generate higher valent more oxidatively active oxides by anodic deposition from an alkaline solution of platinum(IV) in order to proceed further on Wöhler's results mentioned in the present paper. This is why we decided to investigate electrochemical properties and oxidative ability of coating containing this Wöhler's oxide and to start research into the possibility of its preparative use. The results will be presented in this communication.

EXPERIMENTAL

The platinum oxide coatings for voltammetric recordings were deposited by alternating electrolytic polarization from an alkaline PtO_2 solution onto prepared supports. The solutions contained 2·4 to 4·8 mmol $PtO_2.4\,H_2O$ in 10 ml 10% NaOH. Platinum(IV) oxide was prepared from H_2PtCl_6 or K_2PtCl_6 according to procedures given in the literature[6]. The white or yellowish sediment of $PtO_2.4\,H_2O$ was decanted by several portions of distilled water and then dissolved in 10% NaOH giving rise to a yellow solution. The platinum wire electrodes (surface 8–11 mm^2) were purified first in aqua regia before coating, then in concentrated hydrochloric acid and finally thoroughly rinsed with distilled water. Nickel and iron wire electrodes were brushed with fine emory paper both in dry and wet state and rinsed in distilled water before coating. The glassy carbon rod electrode (Carbon Lorraine, France) was cleaned in a 50% H_2SO_4–conc. H_3PO_4 (10 : 1) bath heated to 70°C and then thoroughly rinsed in distilled water.

The wire electrodes were alternately polarized to positive and negative potentials in the above 10% NaOH bath saturated with PtO_2. At ±2·1 to ±2·4 V the oxidative potential of the electrode with the brownish red coating thus formed equalled to +0·62–+0·68 V vs SCE during the anodic polarization. The current density amounted to 150–200 mA cm^{-2}. In order to reach the formation of the brownish red layer sufficient for recording the voltammograms, 5 to 6 one-minute galvanostatic cycles were repeated, consisting of 30 s negative and 30 s positive polarizations. The electrodes with the deposited coatings of platinum oxides were rinsed by distilled water and used then in voltammetric measurements. Between measurements in different solutions the same electrode with the coating was always thoroughly rinsed with distilled water.

Potassium tetrachloroplatinate(II) was prepared by a procedure described in the literature[8], i.e. by reducing potassium hexachloroplatinate(IV).

In voltammetric measurements carried out in a three-electrode system, a saturated calomel electrode was applied as a reference electrode; the experimental arrangement was described in more detail recently[2]. For measuring the pH values of the solutions a glass electrode was applied connected to the pH-meter OP211-1 of the Hungarian producer Radelkis.

The preparative electrolytic oxidations were performed in an undivided all-glass cell[2] equipped with a platinum gauze anode covered by a layer of platinum oxides (having an area of about 1 dm^2) and with an auxiliary electrode of platinum wire. The working electrode was deposited by the above mentioned technique of alternating polarization from 10% NaOH solutions saturated with PtO_2. Unfortunately, in the case of these layer surface areas, neither an increase in the PtO_2 concentration in the deposition bath (to 5–30 mmol PtO_2 in 100 ml), nor the preparation of the electrode surface, nor the choice of the current density (50–200 mA dm^{-2}) led to the formation of the homogeneous brownish red layer. The electrolyte was 0·25M H_2SO_4 with 5–10 vol. % toluene, the temperature of about 80°C. In 0·5M H_2SO_4 the potential of the working electrode was +0·7 V and in 0·25M NaOH the potential was kept at +0·4 V vs SCE.

The current density varied from 200 to 400 mA dm^{-2}. The products were analyzed by means of TLC and GC. The dried toluene phase was applied for analysis. GC was carried out with a CHROM 5 (Laboratorní přístroje, Prague) apparatus, making use of a Chromaton N-AW column containing 15% neopentylglycolsuccinate; FID detection was applied.

RESULTS

The platinum oxide coatings deposited for voltammetric investigations on wire electrodes possessed a reddish brown till dark brown colouration. Neither in alkaline (10% NaOH) nor in strongly acidic solutions (e.g. in 2M H_2SO_4) did they dissolve. Voltammetric recordings with electrodes covered by these coatings yield an anodic and cathodic peak within the pH-region from 0·19 (0·5M H_2SO_4) to 13·20 (0·25M NaOH) (cf. Fig. 1). In 0·5M H_2SO_4 E_{pA} = +0·88 V and E_{pC} +0·57 V was found. In neutral media of a Britton–Robinson buffer pH 6·8 E_{pA} was equal to +0·49 V and E_{pC} to +0·02 V. For a 0·25M NaOH solution E_{pA} = −0·23 V and E_{pC} = −0·35 V was found. In voltammetric recordings extended to more negative values, anodic and cathodic peaks can be also observed which correspond to transformation of PtO_2 (cf. Fig. 6) within the whole pH-region. More attention will be, however, paid to anodic and cathodic peaks in a more positive region which could possibly correspond to the electrochemical transformation of PtO_3. The first voltam-

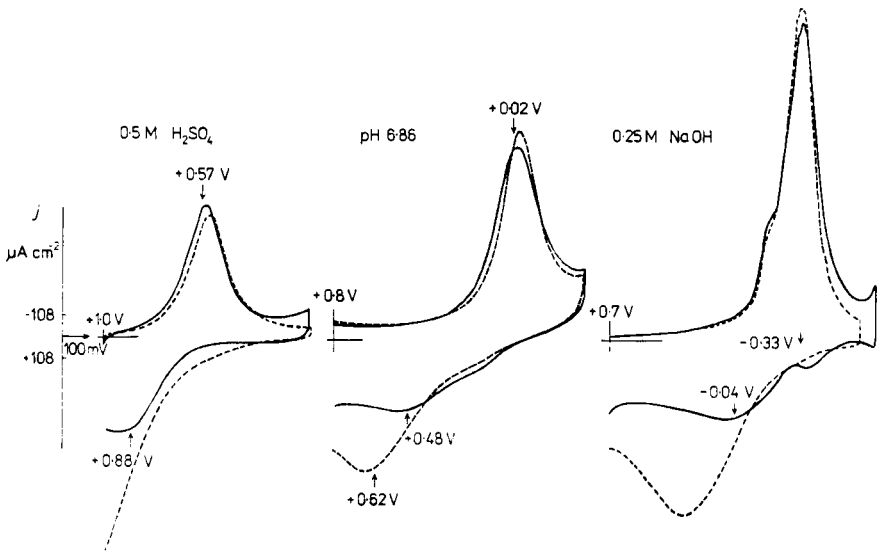

FIG. 1

Voltammetric curves of coatings hydrated oxides PtO_3/PtO_2: full in the given solution; dashed line upon adding toluene; scan-rate 10 mV s^{-1} vs SCE

mogram after the deposition yielded a curve whose cathodic peak was shifted to more negative values as compared to repeated recordings on the same coating. Repeated recordings exhibited a good reproducibility as regards the shapes of the peaks and their position on the potential axis. An addition of toluene to neutral and alkaline media leads to a considerable increase in the height of the anodic peak and to its shift toward more positive potentials (cf. Fig. 1). The increase of the anodic peak in presence of toluene can be repeatedly and reproducibly recorded if polarizing from negative (near to the region of hydrogen evolution) to the positive potentials. An increase of temperature does not change the peak potentials due to the presence of the platinum oxide coatings in the base electrolytes. The addition of toluene causes an increase of the anodic peak and its further development at a potential which is virtually equal to E_{pA} in the base electrolyte (cf. Fig. 2). An increase of temperature both in neutral and acid media causes a similar effect. This is in accordance with the expected increase in the rate of toluene oxidation.

An increase of anodic peaks in voltammograms obtained with a platinum electrode covered by a platinum oxide coating was also observed upon adding xylene, isomeric toluenesulfonamides and some other oxidizable organic educts. However, it was never observed with picolines. A coating consisting of platinum oxides was deposited in a similar manner as that with a platinum wire also on nickel, titanium, iron and glassy carbon. The voltammograms of these coatings were recorded in a 0·25M NaOH solution (cf. Fig. 3). The curves are reproducible and with nickel

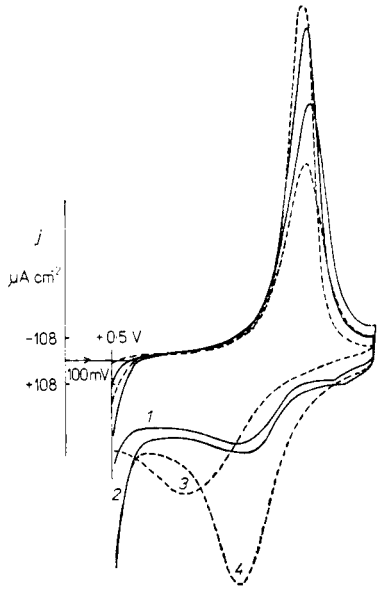

FIG. 2

Voltammetric curves of coatings of hydrated platinum oxides deposited on platinum, recorded in 0·25M NaOH; full curves: *1* temperature 20°C, *2* temperature 80°C; dashed lines: upon adding toluene; *3* temperature 20°C and *4* temperature 80°C; scan-rate 10 mV s^{-1} vs SCE

and titanium supports they exhibit further peaks. Qualitative tests with these coatings upon adding toluene derivatives also prove electrocatalytic oxidative ability, in particular, if deposited on glassy carbon or on iron (cf. Fig. 3c).

In preparative attempts to reach electrocatalytic oxidation with a stirred toluene emulsion in 0·25M NaOH on an imperfect PtO_x-coating (at +0·4 V vs SCE) and at 80°C a 3% yield of benzaldehyde was obtained. The current density was 100–300 mA cm^{-2} and oxygen in small bubbles evolved on the working electrode. In preparative electrolysis of toluene in 0·5M H_2SO_4 at +0·7 V under similar conditions the yield was only 4% benzaldehyde. Figure 4 demonstrates the growth of anodic and cathodic peak currents in voltammograms obtained with 0·25M NaOH solutions and for electrodes coated with platinum oxides.

As in the preceding cases the coatings were prepared by electrolytic deposition from 10% NaOH saturated with colloidal PtO_2. The individual voltammetric curves were recorded after a preceding cathodic polarization of the coating in the potential range from −0·2 V to −0·7 V (vs SCE) in strongly acid 0·5M H_2SO_4 solutions. For each potential to be investigated this polarization lasted 2 min. The linear dependence of the voltammetric peak on the cathodic polarization potential (expressed as current density) is shown in Fig. 5.

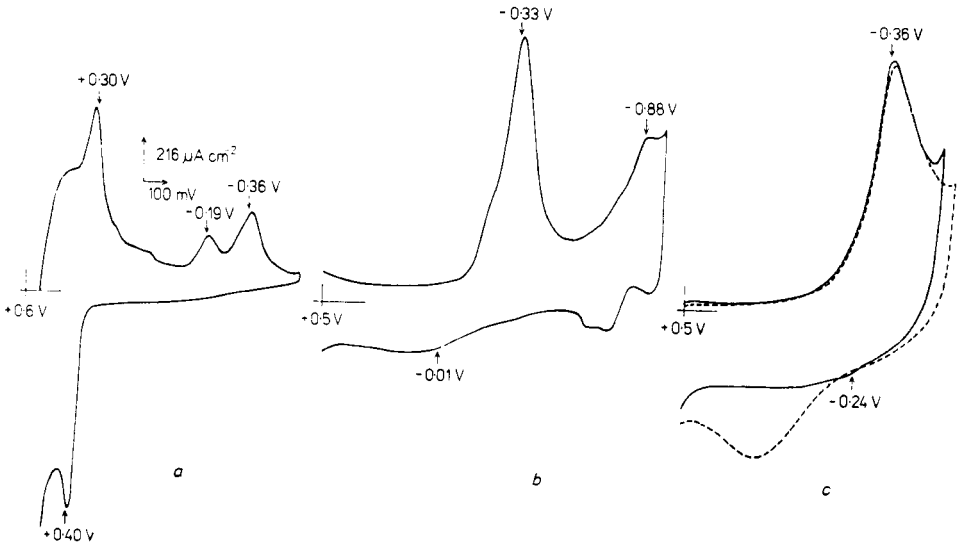

FIG. 3

Voltammetric curves of coatings of hydrated platinum oxides recorded in 0·25M NaOH; deposition on *a* nickel; *b* titanium; *c* iron; dashed line: recorded upon adding toluene; scan-rate 10 mV . . s^{-1} vs SCE

DISCUSSION

The voltammetric curve of the activation bath (alkaline solution of PtO_2) obtained with a bare platinum electrode surface yielded a cathodic voltammetric peak at $E_{pC} = -0{\cdot}80$ V. This value corresponds to the reduction of PtO_2 whose colloidal solution is present here. With reverse polarization no anodic peak was observed under given conditions (scan rate 10 mV s^{-1}). The above peak corresponds therefore to the reduction of Pt(IV) bound in a coordination compound because voltammetric curve results with $K_2Pt(OH)_6$ in alkaline solutions. In addition to this, the voltammogram in the activation bath after a preceding anodic polarization of the platinum electrode exhibited a new cathodic peak at $E_{pC} = -0{\cdot}22$ V. The following cathodic polarization according to the above program led to an approximately three-fold increase in the height of this peak. Several repetitions of the polarization cycle with the deposited ochre brown coating lead to a voltammetric curve with cathodic peaks at $E_{pC} = +0{\cdot}53$ V, $E_{pC} = -0{\cdot}22$ V and $E_{pC} = -0{\cdot}80$ V. No anodic peak was observed when returning back to the starting potential, probably owing to the high volume concentration of PtO_2 in the activation bath. The coated platinum electrode was transferred into an approx. 1% NaOH solution (i.e. 0·25M NaOH) with pH 13·2 and cathodic peaks at $E_{pC} = -0{\cdot}38$ V and $E_{pC} =$

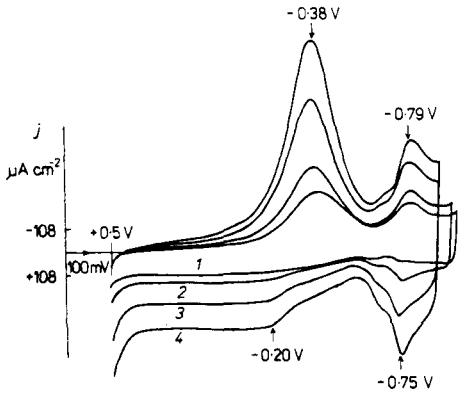

FIG. 4

Voltammetric curves of coatings of hydrated platinum oxides deposited from a NaOH/PtO_2 solution on platinum, recorded in 0·25M NaOH after preparation in 0·5M H_2SO_4 by cathodic polarization at the following potentials: *1* without preparation; *2* $E = -0{\cdot}2$ V; *3* $E = -0{\cdot}4$ V; *4* $E = -0{\cdot}7$ V; scan-rate 10 mV s^{-1} vs SCE

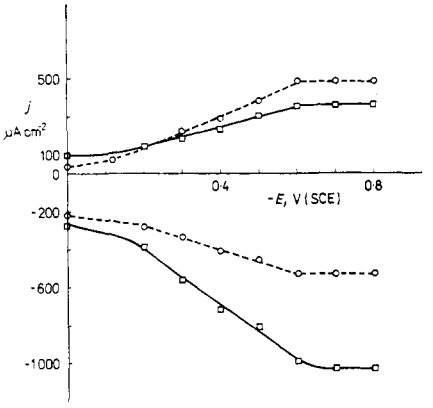

FIG. 5

Dependence of voltammetric peak currents for coatings of hydrated platinum oxides in 0·25M NaOH (after treating by cathodic polarization in 0·5M H_2SO_4) on the applied cathodic potential E; □ anodic and cathodic peak currents for the electrolytic transformation of assumed PtO_3; ○ anodic and cathodic peak currents for the electrolytic transformation of PtO_2

$= -0{\cdot}84$ V were observed (cf. Fig. 6). The shift of E_{pC} values in the following recordings is probably caused by setting free the remains of the bath and the adsorbed oxygen after the deposition of the platinum oxides. The more negative peak in the vicinity of the hydrogen evolution potential ($-0{\cdot}84$ V) is due to the reduction of four-valent platinum. The corresponding anodic peak appears at $E_{pA} = -0{\cdot}70$ V. The new, more positive cathodic peak with $E_{pC} = -0{\cdot}38$ V suggests the possibility of a novel interpretation, i.e. that of the reduction of Pt(VI) in PtO_3 formed in the activation step. The corresponding anodic peak appears at $E_{pA} = -0{\cdot}27$ V. However, this assumption would be in contradiction to the statements e.g. of Kadeřávek and Paseka[3]. Nevertheless, the process could be described as follows: PtO_2 forms a colloidal solution in the activation bath. In the cathodic polarization it may migrate and coagulate at the electrode surface which is also surrounded by sodium ions. It could be partly reduced but the high PtO_2 concentration near the electrode causes reoxidation of the partly reduced layer. In anodic polarization oxygen (in statu nascendi) is developed which could oxidize the deposited PtO_2 to PtO_3. The overall process may be characterized by the following equations:

$$\text{anode: } PtO_2 + 2\,OH^- \xrightarrow[-2e]{NaOH} PtO_3 + H_2O\,, \qquad (1)$$

$$\text{cathode: } 2\,Na^+ + PtO_2 + H_2O \xrightarrow[+2e]{NaOH} 2\,NaOH + PtO\,, \qquad (2)$$

$$\text{coating on the support: } PtO + PtO_3 \rightarrow 2\,PtO_2\,. \qquad (3)$$

PtO is rather unstable and is readily oxidized to PtO_2 if exposed to air. K_2PtCl_4, prepared as standard[8], containing Pt(II), yielded anodic peaks in voltammetry at a platinum electrode. With respect to the easy deposition of PtO in neutral or alkaline media, Pt(II) peaks at a platinum electrode were only recorded with acid media. The E_{pA} values (vs SCE) are $+0{\cdot}65$ V (in 0·5M H_2SO_4), and 0·48 V at pH 1·2 and 0·36 V at pH 3·70 (in Britton–Robinson buffer).

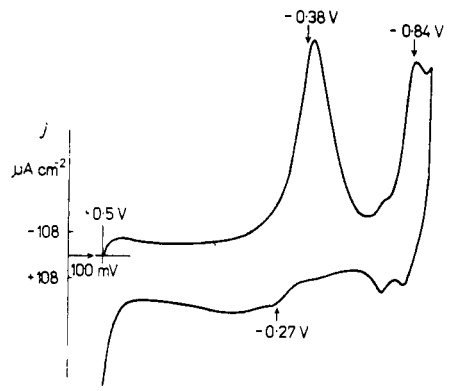

FIG. 6

Voltammetric curve of the coating formed by hydrated platinum oxides deposited from a 10% NaOH/PtO_2 solution on platinum; recorded in 0·25M NaOH; scan-rate 10 mV . . s^{-1} vs SCE

The comparison of these peak potentials with E_{pA} values recorded in the corresponding acid media with coated platinum electrodes points to a certain agreement. Voltammetric recordings of the deposited coatings of platinum oxides on a platinum support in strongly alkaline media exhibit the lowest difference between the anodic and the cathodic peak potential ($\Delta E_p = 90-110$ mV). Such a peak couple, corresponding possibly to the transformation processes of PtO_3 has a partly reversible character. In more alkaline media (5–10% NaOH) this feature is even more pronounced.

The cathodic polarization of the deposited coatings in strongly acidic media (e.g. 0·5M H_2SO_4) brings about an enhancement of voltammetric peaks. The colouration of the originally golden-yellow or reddish brown coating turns black. Figure 4 demonstrates this behaviour of a layer deposited from a PtO_2 solution in 10% NaOH. When polarizing the coating from −0·2 to −0·7 V in strongly acidic media both peaks are enhanced. A coating consisting of platinum oxides was also deposited on platinum from a PtO_2 solution in approx. 10% aqueous solution of $N(Bu)_4OH$. It possessed a silver-gray colour and its voltammogram in 0·25M NaOH led only to low cathodic and scarcely visible anodic peaks which, as regards potentials could correspond again to the transformation of PtO_3 and PtO_2. Following the cathodic polarization of this coating at −0·6 V in 0·5M H_2SO_4 only a small enhancement was observed of peaks yielded by the coating if recorded in 0·25M NaOH. This behaviour of platinum oxides deposited from PtO_2 solutions in alkali hydroxides points to the fact that a certain quantity of NaOH is bonded to the oxides in the coating. Cathodic polarization causes irreversible desorption of NaOH which gives rise to the corresponding salt in the surrounding acid. In this way probably a displacement of alkali metal ions occurs from the deeper layers of the platinum oxides: this results in a growth of peak currents in voltammetry. This interpretation is not at variance with the finding of Wöhler[6] who for an electrolytically prepared PtO_3 (from 2M KOH) reports a composition $3\,PtO_3.K_2O$, basing on analytical results. He also describes a colour change from yellow-green to red-brown under the influence of 0·5M CH_3COOH, which should suffice for setting free alkali metal ions from $PtO_3.K_2O$. We agree that the colour appearance of the coating possibily containing PtO_3 depends to a higher degree on the contents of the intercalated NaOH than on dispersity, water contents and state of oxidation in PtO_x. Such an intercalation of ions from the electrolyte into the host lattice of the electrode material is not an isolated case, a similar example has been described e.g. by Beck and Krohn[9].

An addition of toluene (Fig. 1) in voltammetry with coatings in the studied electrolytes does not change the height of the cathodic peak but it strongly enhance the anodic peak and shifts its E_{pA} to more positive potentials.

Upon adding ethanol in alkaline, neutral and acid media, a single, high anodic peak appeared with both directions of the voltage-scan. This points to a recording on coatings consisting of platinum oxides obtained with additions of intermediates

of toluene oxidation such as benzyl alcohol or benzaldehyde; this behaviour confirms a much easier oxidation as compared to that of toluene.

It is evident that for the oxidation of toluene and of its derivatives the presence of the oxidatively active form of platinum oxide is indispensable.

As regards the influence of the support on the deposited coatings, glassy carbon represents an inactive support because the platinum oxides coatings deposited on it in the usual manner give in all solutions only peaks essentially equal to those obtained with coatings deposited on platinum.

When the coating consisting of platinum oxides was deposited on a nickel support two couples of anodic-cathodic peaks (Fig. 3) resulted in alkaline media (pH 13·20). The more positive high cathodic–anodic reversible couple corresponds to the system NiO(OH); the peak potentials of the more negative couple of peaks are very close to the corresponding potentials of the coating of platinum oxides deposited on platinum under identical conditions. When comparing the peak potentials for NiO(OH) deposited on platinum whith those on a nickel support a fair agreement has been observed: $E_{pA} = +0{\cdot}40$ V/$E_{pC} = +0{\cdot}28$ V vs the values for the deposit on platinum: $E_{pA} = +0{\cdot}35$ V/$E_{pC} = +0{\cdot}26$ V.

A black layer of platinum oxides is usually deposited on a titanium support; its voltammogram, recorded in 0·25M NaOH exhibits peaks with $E_{pC} = -0{\cdot}33$ V and $E_{pA} = -0{\cdot}01$ V; a more negative couple appears at $E_{pC} = -0{\cdot}88$ V and $E_{pA} = -0{\cdot}65$ V (cf. Fig. 3*b*).

The red-brown coating of active platinum oxides deposited on iron yielded a voltammogram in 0·25M NaOH (cf. Fig. 3*c*) the peak potentials of which corresponded to the values obtained with platinum oxides deposited on a platinum support. The dashed curve (Fig. 3*c*) recorded after adding toluene results in an increase of the anodic peaks: this confirms oxidative activity of this coating.

In preparative experiments we did not succeed in covering the prepared platinum grid with an equally active reddish brown or ochre-brown coating as in case of electrodes for voltammetry. The deposited black-brown coating applied in experiments to electrooxidize toluene preparatively, only confirmed the formation of benzaldehyde at increased temperature (80°C) both in strongly acidic (0·5M H_2SO_4) and in alkaline media (0·25M NaOH). Nevertheless, the yield as well as the current efficiency are rather low.

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