

Electrooxidation of β -D(+)-glucose on bare and u.p.d. modified platinum particles dispersed in polyaniline

A. KELAIPOULOU, A. PAPOUTSIS, G. KOKKINIDIS

Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

W. T. NAPPORN, J.-M. LEGER, C. LAMY

UMR 6503, Equipe Electrocatalyse, Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers, France

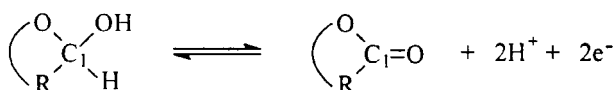
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Platinum particles dispersed in a polyaniline film (PAni/Pt) provide a better catalyst than smooth Pt for the electrooxidation of β -D(+)-glucose in perchloric acid aqueous solutions. The Pt particles are less sensitive to poison formation than smooth platinum. Their catalytic activity is influenced by modification with underpotential deposition (u.p.d.) of thallium, lead or bismuth. Up to 0.4 V vs RHE the Pt particles show a better activity than u.p.d.-modified platinum particles. However, above 0.4 V the u.p.d.-modified particles are more active than bare Pt particles. Underpotential deposition of cadmium inhibits the electrooxidation of β -D(+)-glucose. The morphology and the nature of the metallic dispersion were examined by transmission electron microscopy.

Keywords: electrooxidation, β -D(+)-glucose, underpotential deposition, Pt particle catalysts, polyaniline

1. Introduction

Interest in the investigation of the electrochemical oxidation of glucose stems from the possibility of using this monosaccharide as a fuel in an implantable biofuel cell which could serve as the power source of an artificial heart or a cardiac pacemaker or in developing a glucose sensor in relation to an artificial pancreas [1–5]. The electrocatalyst used for this oxidation process is mainly platinum [6–20], either polycrystalline or as single crystals. Gold and other noble metal electrodes have also been used but only in alkaline solutions, where they exhibit significant catalytic activity [21–25]. According to these studies, glucose, in the form of a closed ring (α - or β -anomer), undergoes oxidation to produce glucono- δ -lactone according to the overall two-electron reaction [11]:



The glucono- δ -lactone obtained undergoes hydrolysis to yield gluconic acid, which is the main oxidation product. However, many other products were detected [26]: glucaric, glucuronic, tartaric, glyoxylic, oxalic, glycolic and formic acids. CO_2 was also proposed as the final product [27] of any chemisorbed species formed. During the several paths of the glucose electrooxidation, variable amounts of reactive intermediate molecules are produced depending on the electrode potential. The less reactive

ones are strongly adsorbed molecules of gluconolactone-type which can be removed from the electrode surface only after oxidative decomposition at very positive potentials. Such intermediates, the so called poisoning species, reduce the electrode performance by blocking active sites, particularly for platinum electrodes in acid solutions. One other poison species which can be detected in small amounts, during the adsorption of glucose is adsorbed CO as observed by *in situ* Infrared spectroscopies [19, 20, 28, 29]. The presence of CO is proof that the adsorption of glucose is partially dissociative, even if the main path is the formation of gluconolactone. One of the suitable methods of diminishing poisoning effects is the modification of the Pt surface by underpotential deposited (u.p.d.) layers of Pb, Tl and Bi [25, 26, 30–32].

Recent developments in the preparation of nanostructured metal particles and their dispersion in porous materials have opened up the possibility of simple preparation of high performance electrocatalysts for technologically important reactions. Thus, effective electrocatalysts are now routinely prepared by dispersing metal nanoparticles in conducting polymer films [33–53]. It has been shown that such modified electrodes with Pt or Pt-based multimetallic assemblies are better catalysts than smooth platinum for the oxidation of some organic fuels. So far, only small organic molecules (e.g., CH_3OH [37, 39, 41, 42, 46, 47, 50], HCHO [46, 47], HCOOH [46, 47, 51], $\text{CH}_3\text{CH}_2\text{OH}$ [50], $\text{CH}_2\text{OHCH}_2\text{OH}$ [53]) have been studied. Therefore, it would be interesting to extend

the use of such electrodes to the study of larger molecules which are also important in fuel cell technology. Such a fuel is glucose. Furthermore, since the underpotential deposition of heavy metals enhances the catalytic activity of smooth platinum for the oxidation of glucose [25, 26, 30–32], it was decided to also include the effect of u.p.d. in this study. The aim is to investigate the influence of the particle size of the three-dimensional nanostructured electrode on the formation of underpotential deposited layers and their influence on the kinetics of glucose electrooxidation.

In this paper we report the electrooxidation of β -D(+)-glucose on pure and u.p.d. modified platinum particles finely dispersed in a polyaniline film in aqueous acidic solutions. Transmission electron microscopy (TEM) was employed to give information about the morphology and nature of the deposited electrocatalyst particles.

2. Experimental details

A glassy carbon disc or a platinum bead was used as working electrodes. Before each experiment, the disc electrodes were mechanically polished using emery paper and then electrochemically activated using preelectrolysis. The platinum bead was first pretreated by flame and then electrochemically activated. The modification of the carbon disc electrodes was performed in two steps: (a) electropolymerisation of aniline by potential cycling ($v = 50 \text{ mV s}^{-1}$) between 0 and 0.98 V vs RHE in a $0.5 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M}$ aniline aqueous solution [54], (b) electrodeposition of platinum potentiostatically at 0.1 V vs RHE.

The thickness of the polymer film was estimated from the height of the first anodic peak of the cyclic voltammogram of polyaniline in base electrolyte (aqueous H_2SO_4 0.5 M) [55]. The polymer film used was $0.5 \mu\text{m}$ thick.

For platinum deposition, the solution employed was $0.5 \text{ M H}_2\text{SO}_4 + 2 \times 10^{-4} \text{ M K}_2\text{PtCl}_6$. The mass of platinum incorporated was calculated from the charge passed during electrolysis. After each experiment polyaniline with the incorporated metallic particles was removed from the electrode surface by dissolution in chromic + sulphuric acid.

For the u.p.d., the β -D(+)-glucose solution also contained dissolved salts of Tl(I), Pb(II), Cd(II) or bismuth(III) in several concentrations ranging from 10^{-5} to 10^{-3} M . The cell used for the voltammetric study of β -D(+)-glucose reactivity was double walled and thermostated at $25 \pm 0.1 \text{ }^\circ\text{C}$. A Hg/Hg₂SO₄/Na₂SO₄ (sat.) electrode and a glassy carbon sheet served as the reference and the counter electrode, respectively. The solutions were thoroughly deoxygenated by purging the electrochemical cell with ultrapure nitrogen. Electrode potentials are given in the reversible hydrogen electrode (RHE) scale.

Solutions were prepared using ultrapure water (Millipore Milli-Q system) and reagents from Merck (HClO₄ and H₂SO₄, 'suprapur', Fluka (Bi₂O₃ and Pb(ClO₄)₂, 'purum'), Alfa Johnson Matthey

(K₂PtCl₆), Strem Chemicals (Cd(ClO₄)₂, TiClO₄) and Sigma (β -D(+)-glucose with up to 3% α -anomer). Aniline (Merck, 'pro analysi') was further purified before use by vacuum distillation.

The electronic set-up consisted of a potentiostat (Wenking 7529 68FR05), a voltage scan generator (Wenking VSG 72), and a Linseis LY 17100 X-Y recorder. For transmission electron microscopy (TEM) observations, Au (300 mesh) grids supplied by Agar Scientific Ltd were used as substrates for the polymerization of aniline and deposition of platinum. The grids were activated by applying a continuous sweep ($v = 1 \text{ V s}^{-1}$) between hydrogen evolution and just before oxygen evolution in 0.1 M HClO_4 solution until the cyclic voltammograms (0.1 V s^{-1}) obtained had the known shape for Au. The TEM study was performed with a Joel 100CX microscope operating at 120 kV.

3. Results and discussion

3.1. Electrooxidation of β -D(+)-glucose on smooth Pt and Pt particles dispersed in polyaniline

The voltammetric behaviour of β -D(+)-glucose on smooth platinum in aqueous 0.1 M HClO_4 solution is given in Fig. 1. During the positive scan three main peaks appear corresponding to the oxidation of glucose molecules on different platinum states: peak (I) in the hydrogen adsorption region, peak (II) just before the end of the double layer (d.l.) region and peak (III) in the range where the Pt surface is fully covered by oxides. In accordance with previous observations [8, 30, 31], peak (I) is adsorption controlled, while peaks (II) and (III) display kinetic character. The currents obtained in the d.l. region are

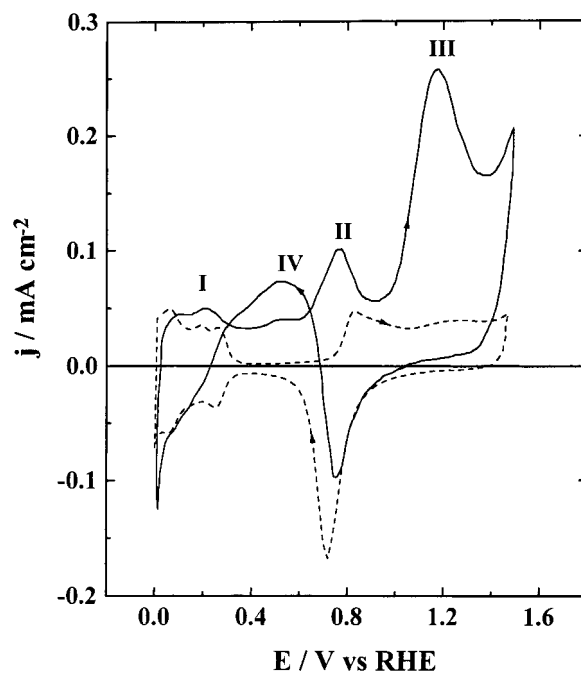


Fig. 1. Voltammograms for the oxidation of β -D(+)-glucose (0.1 M) on a Pt bead in 0.1 M HClO_4 . $|dE/dt| = 50 \text{ mV s}^{-1}$. The dashed line corresponds to the supporting electrolyte.

very low. It is generally believed [11, 12] that gluconolactone or adsorbed CO species (produced in the hydrogen adsorption region by dehydrogenation of glucose) blocks the active sites of platinum, so that bulk oxidation of glucose occurs on the remaining free surface sites. During the negative scan one oxidation peak (IV) followed by a hump appears immediately after the reduction of the Pt oxides. The direct oxidation product of all four peaks is gluconolactone which is unstable in aqueous solutions and undergoes hydrolysis to produce gluconic acid.

The voltammogram of β -D(+)-glucose oxidation on platinum dispersed in polyaniline is shown in Fig. 2 along with the voltammogram of the PANi/Pt electrode in the supporting electrolyte alone. To avoid overoxidation of the polymer film, the anodic potential limit was kept below 1.07 V. As can be seen, the voltammogram of glucose oxidation obtained on PANi/Pt is quite different from that obtained on smooth platinum, indicating the dependence of glucose electrooxidation on the morphology of the Pt electrocatalyst. The first peak in the hydrogen region cannot be observed anymore and, instead of the second peak at the end of the d.l. region, a much higher peak appears in the d.l. region (at potentials less positive by around 300 mV). As on smooth platinum, during the negative scan an oxidation peak also appears in the d.l. region.

The PANi/Pt electrode is much more active than smooth platinum. Much higher currents are obtained at less positive potentials. This may be attributed, on the one hand, to the large surface area of the particles and, on the other hand, to the fact that the Pt nanoparticles are less sensitive to poisoning from adsorbed species. The latter is supported by the fact

that the maximum current density on dispersed platinum is observed in the d.l. region, whereas in the case of smooth platinum, the current is almost completely suppressed due to the strong adsorption of intermediates.

The present results clearly show the influence of the size of the electrocatalyst particles of the nanostructured electrode on the kinetics of the electrooxidation of β -D(+)-glucose. It should be noted that structural effects upon the kinetics of glucose oxidation arise not only from the particle size but also from the surface structure of the electrode, as was postulated in earlier studies on single crystal electrodes [17, 23, 24, 32]. Platinum single crystal electrodes show much higher activity for glucose electrooxidation than polycrystalline Pt [32], particularly the Pt(1 1 1) face which is less sensitive to poison formation.

Although chemisorption of intermediates on the Pt particles dispersed in polyaniline appears to be less intense than on smooth platinum, poisoning effects are still significant for glucose oxidation on the PANi/Pt electrode. By reversing a cathodic sweep at less negative potential limits on the PANi/Pt electrode, the current due to the oxidation of glucose in the subsequent anodic sweep decreases significantly. Figure 3 shows voltammograms of β -D(+)-glucose oxidation starting from different potential lower limits. The decrease of the current with the shift of the starting potential towards more positive values is explained by the fact that at more positive potentials adsorption of glucose is accelerated producing the strongly adsorbed lactone-type species and, therefore, more rapid poisoning of the electrode surface does occur [31].

Each cycle is recorded after a five minute stay at the lower potential limit as penetration and diffusion

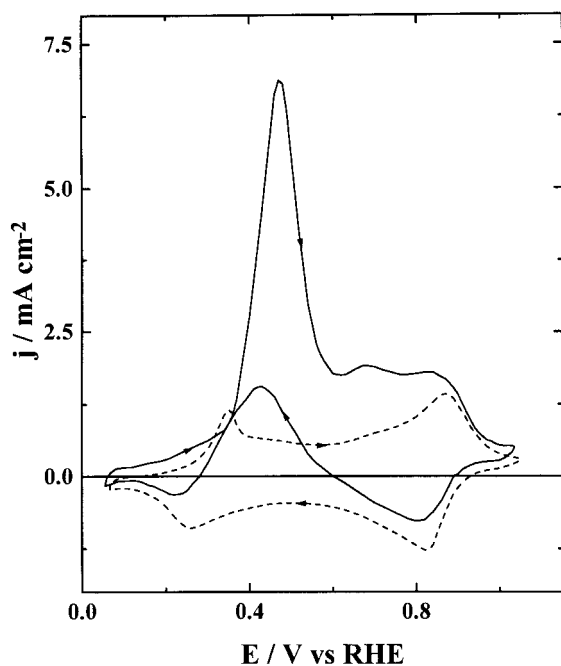


Fig. 2. Voltammograms obtained on a PANi/Pt (2.7 mg cm^{-2}) electrode in 0.1 M HClO_4 in the absence (---) and presence (—) of $0.1 \text{ M } \beta$ -D(+)-glucose $|dE/dt| = 5 \text{ mV s}^{-1}$.

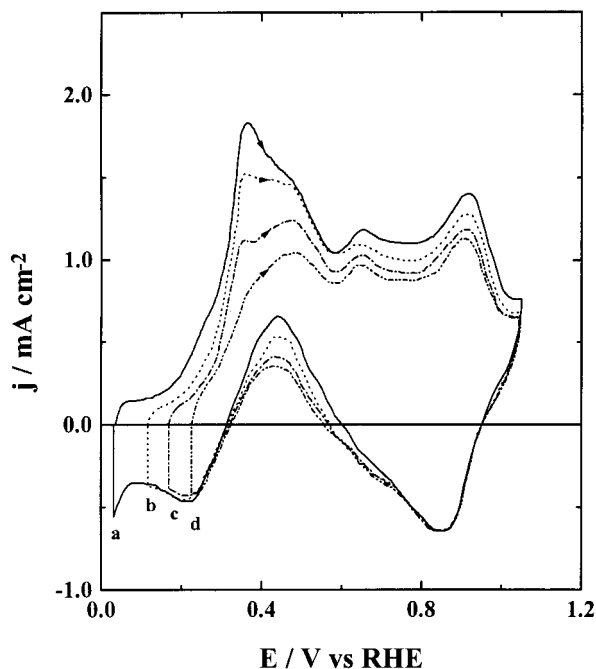


Fig. 3. Voltammograms for the oxidation of β -D(+)-glucose (0.1 M) on a PANi/Pt (1.0 mg cm^{-2}) electrode in 0.1 M HClO_4 obtained for different cathodic limits (V vs RHE): (a) 0.03, (b) 0.13, (c) 0.18, (d) 0.24. $|dE/dt| = 5 \text{ mV s}^{-1}$.

of glucose through the polymer film is a slow step. Under rotating conditions and for low rotation rates the height of the current peaks increases with the rotation rate in such a manner that the j^{-1} against $\omega^{-1/2}$ dependence (Koutecky–Levich analysis) gives straight lines. The intercept of the j_p^{-1} against $\omega^{-1/2}$ plots is proportional to the film thickness, indicating that transport of glucose through the film is one of the controlling factors. This suggests that the platinum particles are not concentrated on the polymer-solution interface but dispersed in a three-dimensional way in the polymer matrix, which is in agreement with earlier studies [37].

The current densities of β -D(+)-glucose oxidation are affected by the mass of the electrodeposited platinum. For the peak that appears first in the positive direction of the sweep, the variation of current density with the Pt loading is given in Fig. 4. It increases with the mass of the deposited metal until a loading of around 2.4 mg cm^{-2} , where it attains a limiting value of about 6.2 mA cm^{-2} . Thereafter, the extra platinum added does not increase the active electrode surface area but the catalyst undergoes a lower degree of dispersion. The current densities were calculated after subtracting the background current and considering as electrode surface the geometric surface area of the supporting electrode.

A closer observation of the electrode morphology by TEM showed that platinum is dispersed homogeneously in groups of three-dimensionally dispersed particles as depicted in Fig. 5. The corresponding diffraction pattern shows the diffraction rings of the platinum (Table 1) particles. The order of magnitude of the mean diameter of the metallic particles is much smaller than one micrometer and it seems that it does

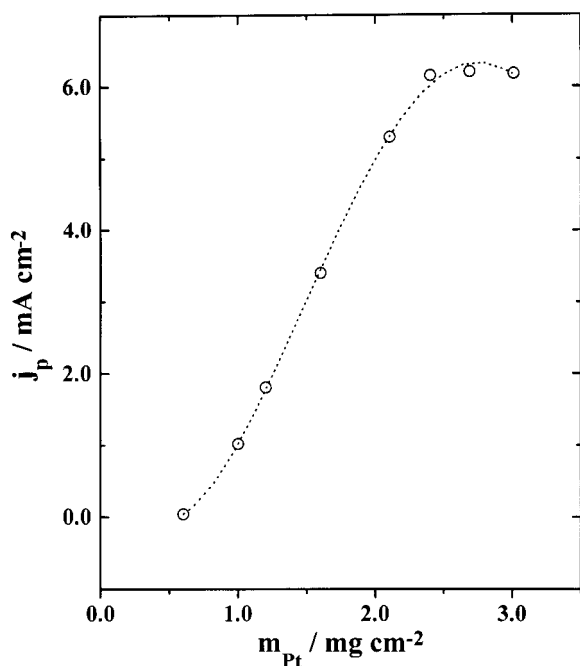


Fig. 4. Plot of the current density of the first oxidation peak of β -D(+)-glucose on PANi/Pt in 0.1 M HClO_4 against the platinum loading.

not change significantly with the Pt mass incorporated for the platinum loadings employed. During electrodeposition, platinum is used more for the formation of new platinum particles and less for the growth of the already existing metallic nanoparticles at least for metal loadings lower than around 2 mg cm^{-2} .

In agreement with earlier studies [53], the activity of these electrodes exhibits remarkable stability against both use and storage in the absence of extreme conditions (mechanical or electrical).

3.2. Electrooxidation of β -D(+)-glucose on PANi/Pt/ M (u.p.d.) systems ($M = \text{Tl, Pb, Bi, Cd}$)

The catalytic activity of platinum nanoparticles dispersed in polyaniline for glucose oxidation is influ-

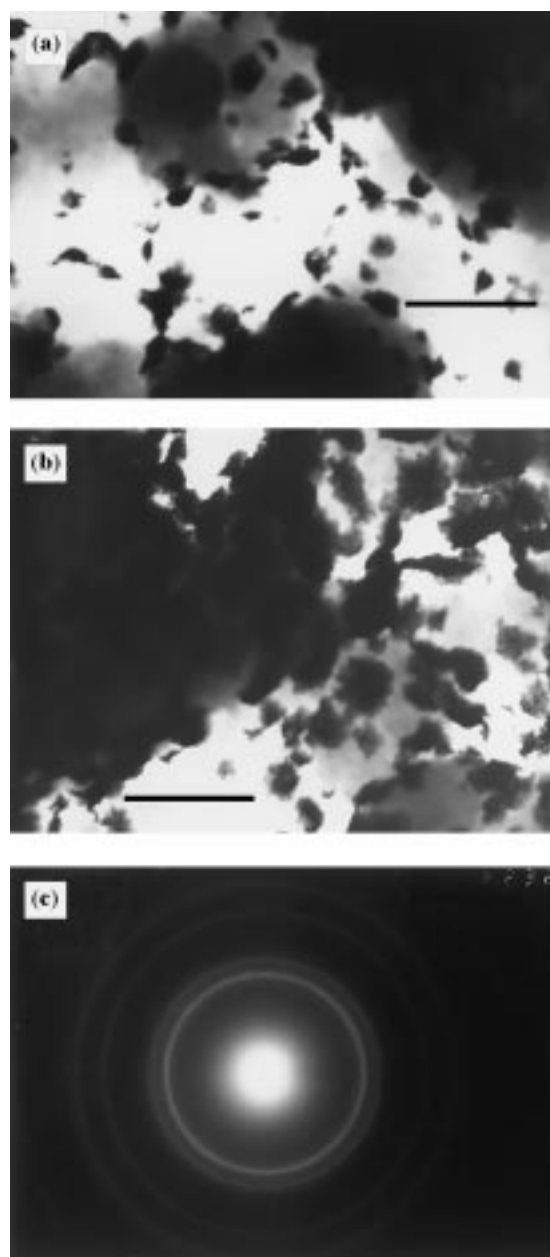


Fig. 5. TEM images of a PANi/Pt electrode for low (a) and (b) three times higher platinum loading with the corresponding diffraction pattern (c). Bar = $0.3 \mu\text{m}$ for both micrographs.

enced by the underpotential deposition of heavy metals. Figures 6, 7 and 8 show the voltammograms of the electrooxidation of β -D(+)-glucose on the PANi/Pt electrodes modified by underpotential deposited layers of Tl, Pb and Bi, respectively.

As can be seen, the adatoms cause a minor negative catalytic effect as regards the oxidation potential. The onset of oxidation and the corresponding peak potentials are slightly shifted towards more positive values. On the other hand, the adatoms cause a notable increase of the peak current density. The maximum catalytic activity appears in the range from 0.3 to 0.6 V. Maximum currents were obtained with concentrations of heavy metal ions in solution of 5×10^{-4} M for Pb^{2+} and 10^{-4} M for Tl^+ and Bi^{3+} . The u.p.d. of cadmium was also tested but unlike the other adatoms it inhibited glucose oxidation.

The data of the influence of u.p.d. on glucose oxidation on the PANi/Pt electrodes are compared with those previously described for smooth platinum either as polycrystalline [30, 31] or as single crystals [32]. The behaviour on PANi/Pt appears to be similar

Table 1. d_{hkl} Values of Pt (from 'Power Data Files' [56]) compared with measured d_{obs} values (from the diffraction pattern)

hkl	$d/\text{\AA}$	$d_{obs}/\text{\AA}$
111	2.265	2.26
200	1.962	1.97
220	1.387	1.39
311	1.1826	1.18
222	1.1325	
400	0.9808	
331	0.9000	
420	0.8773	

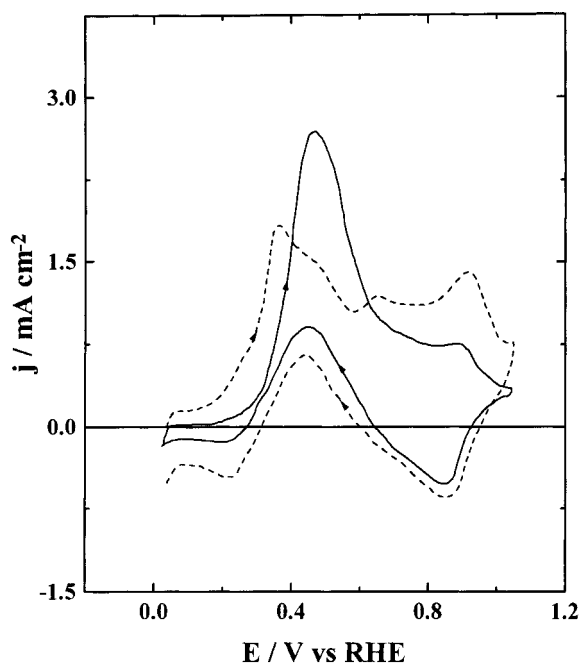


Fig. 6. Voltammograms for the oxidation of β -D(+)-glucose (0.1 M) on a PANi/Pt (1.0 mg cm^{-2}) electrode in the absence (---) and presence (—) of 10^{-4} M TlClO_4 in 0.1 M HClO_4 . $|dE/dt| = 5 \text{ mV s}^{-1}$.

to that observed on the Pt(hkl) single crystal electrodes rather than on polycrystalline platinum. On Pt(hkl) a positive catalytic effect was also observed only for the current density [32], while on polycrystalline Pt significant enhancement in the electrocatalytic activity appeared both in terms of current density and potential [30, 31]. Table 2 gives peak current densities and peak potentials for the oxida-

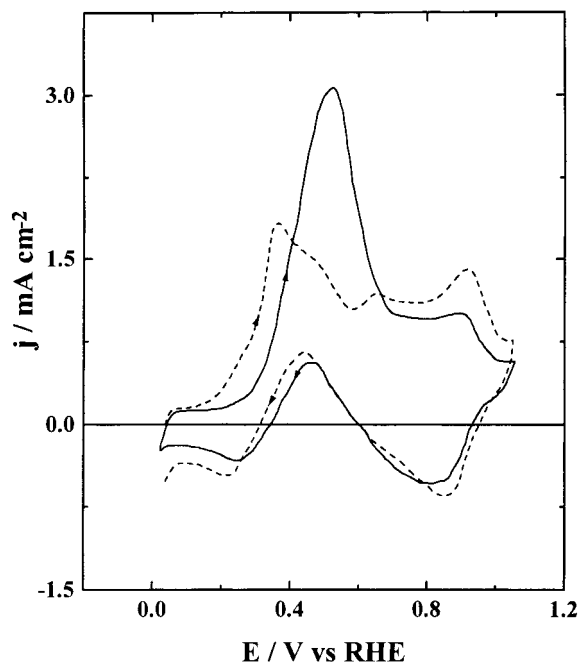


Fig. 7. Voltammograms for the oxidation of β -D(+)-glucose (0.1 M) on a PANi/Pt (1.0 mg cm^{-2}) electrode in the absence (---) and presence (—) of 5×10^{-4} M $\text{Pb}(\text{ClO}_4)_2$ in 0.1 M HClO_4 . $|dE/dt| = 5 \text{ mV s}^{-1}$.

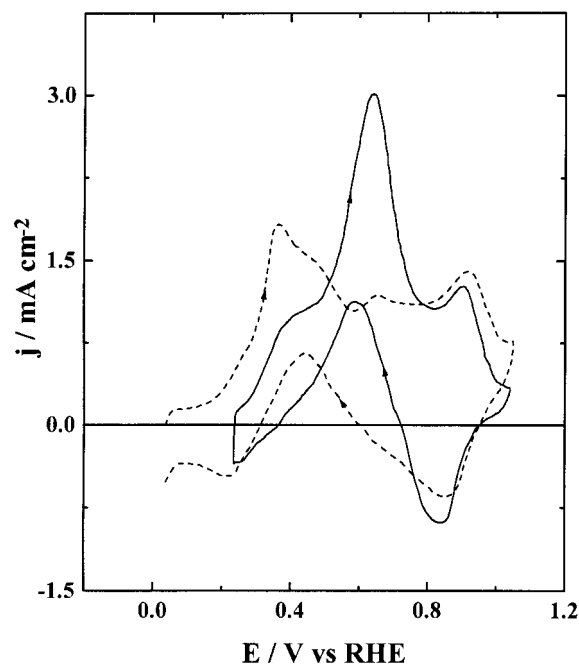


Fig. 8. Voltammograms for the oxidation of β -D(+)-glucose (0.1 M) on a PANi/Pt (1.0 mg cm^{-2}) electrode in the absence (---) and presence (—) of 10^{-4} M $\text{Bi}(\text{ClO}_4)_3$ in 0.1 M HClO_4 . $|dE/dt| = 5 \text{ mV s}^{-1}$.

Table 2. Peak current densities and peak potentials for the electro-oxidation of β -D(+)-glucose on bare and u.p.d. modified Pt(poly), PANi/Pt and Pt(100) electrodes

Values in brackets indicate the ratio of j_p with and without adatoms and the difference of E_p with and without adatoms

Electrode	$j_p/\text{mA cm}^{-2}$	E_p/V_{RHE}
Pt(poly)*	0.22	0.80
Pt/Tl(u.p.d.)	1.08 (4.91)	0.57 (−0.23)
Pt/Pb(u.p.d.)	1.04 (4.73)	0.63 (−0.17)
Pt/Bi(u.p.d.)	1.18 (5.36)	0.71 (−0.09)
PANi/Pt (1.0 mg cm ^{−2})	1.02	0.39
PANi/Pt/Tl(u.p.d.)	2.06 (2.02)	0.47 (+0.08)
PANi/Pt/Pb(u.p.d.)	2.51 (2.46)	0.52 (+0.13)
PANi/Pt/Bi(u.p.d.)	2.40 (2.35)	0.64 (+0.25)
Pt(100) †	0.78	0.35
Pt(100)/Tl(u.p.d.)	3.06 (3.92)	0.58 (+0.23)
Pt(100)/Pb(u.p.d.)	1.33 (1.70)	0.55 (+0.20)
Pt(100)/Bi(u.p.d.)	0.67 (0.86)	0.71 (+0.36)

* Data from [31].

† Data from [32].

tion of glucose in aqueous perchloric acid solutions on bare and u.p.d.-modified Pt(poly), PANi/Pt and on the Pt(1 0 0) crystal face (chosen among the three low index faces). Values of j_p and E_p for PANi/Pt and PANi/Pt/M(u.p.d.) were derived from the corresponding curves after subtracting the currents in the absence of glucose. It should also be noted that the cyclic voltammograms for Pt(poly) [31] and Pt(1 0 0) [32] were taken with 50 mV s^{−1} and not with 5 mV s^{−1}.

As mentioned above, the Pt nanoparticles appear to be less sensitive to poison formation than the polycrystalline smooth Pt surface. Therefore, a smaller improvement of the electrocatalytic activity of the nanostructured material is to be expected, considering that the adatoms increase the catalytic activity of platinum, in fact, by preventing poison formation according to the well known ‘third body’ mechanism [57, 58]. Similar conclusion was drawn from an earlier study [32] concerning the electrocatalytic oxidation of glucose on Pt single crystal electrodes. The adatom effect was less important for the Pt(1 1 1) plane which was the least sensitive to poisoning and the most active one in the absence of adatoms.

The long-term stability of the PANi/Pt/M(u.p.d.) electrodes for glucose electrooxidation was examined by recording potentiostatic current–time curves at the peak potentials. It was found that the electrode with the Pb(u.p.d.) adatom layer is the most stable one and that the stability decreases in the order Pt/Pb(u.p.d.) > Pt/Tl(u.p.d.) > Pt/Bi(u.p.d.) > Pt.

In conclusion, platinum dispersed in a polyaniline film is a better catalyst than smooth Pt for the electrooxidation of β -D(+)-glucose in aqueous perchloric acid solutions. The catalytic activity of the Pt nanoparticles is influenced by modification with underpotential deposited layers of Tl, Pb and Bi. Up to 0.4 V the Pt particles show a better activity than upd-modified platinum particles. Only above 0.4 V

the u.p.d.-modified particles are more active than the bare Pt particles. Therefore, for glucose fuel cells the PANi/Pt electrode without adatoms should be the best catalyst. The Pt particles are less sensitive to poison formation than smooth Pt and, as a result, the effect of u.p.d appears to be less important compared to that reported in the literature for smooth polycrystalline Pt surfaces. Apparently, the particle size of the nanostructured material influences the kinetics of glucose electrooxidation. However, to draw any concrete conclusion on this matter, the influence of particle size on the oxidation of glucose should be studied more systematically.

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