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Methanol oxidation at platinized lead coatings prepared by a two-step electrodeposition–electroless deposition process on glassy carbon and platinum substrates

S. Papadimitriou^a, A. Tegou^a, E. Pavlidou^b, G. Kokkinidis^a, S. Sotiropoulos^{a,*}

^a Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece ^b Department of Physics, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece

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Abstract

Platinized lead deposits, Pt(Pb), have been formed on glassy carbon (GC) and platinum electrodes by a two-step process, whereby a controlled amount of Pb was electrodeposited onto the substrates and was subsequently coated with a thin Pt layer upon immersion of the Pb/GC or Pb/Pt electrodes into a chloroplatinic acid solution. The spontaneous surface replacement of Pb by Pt resulted in Pt(Pb)/GC or Pt(Pb)/Pt electrodes which consisted of dispersed Pt(Pb) particles and displayed typical Pt surface electrochemistry in deaerated acid solutions. When tested as methanol oxidation anodes, these electrodes exhibited enhanced electrocatalytic activity both during voltammetric and constant potential experiments. This behaviour is attributed to an electronic effect of the underlying Pb onto the Pt surface layer. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Platinum catalysts; Electroless deposition; Lead electrodeposition; Methanol oxidation

1. Introduction

Most fuel cell electrocatalysts are formed by chemical methods, usually impregnation of high surface area carbons with the metal ion, followed by reduction with an appropriate agent ([1] and references therein). Electrodeposition of precious metals on electrode substrates avoids the use of reducing agents and provides accurate control of catalyst loading but requires relatively large solution volumes and high metal ion concentrations.

Recently, a new method for the preparation of precious metal coatings has been proposed whereby the surface layer of a less precious metal (Ru, Cu, Pb and Ti) is replaced by the precious metal catalyst (Pt and Pd) by spontaneous electroless exchange of the former by the latter, upon immersion into a complex solution of Pt or Pd ions [2–10]. In some cases the metal layer to be replaced (mainly Cu or, in one case, Pb too) had been freshly electrodeposited onto another electrode substrate, usually Au [4,8–10]. In the work of Adzic and co-workers a Cu mono-

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layer had been deposited on the electrode substrate [4,9] while in that of Kokkinidis and co-workers the layer of the metal to be exchanged (Cu or Pb) has been a few hundred monolayers thick [8,10]. This method has an interesting potential for the preparation of electrocatalysts both from a practical and a theoretical point of view. First, it minimises the amount of precious metal used to that of a thin surface layer. Second, unlike other bimetallic catalysts where the second component is exposed to the reaction medium too (either in the form of an adatom or as a surface alloy component), this type of catalyst allows the study of the electronic effect alone of the second component underlayer to the precious catalyst overlayer.

In all related studies the substrate, onto which the metal layers to be exchanged (Cu or Pb) have been electrodeposited, has been other than a carbon material (the standard support of commercial electrocatalysts). Also, although the resulting electrodes have been tested as electrocatalysts for oxygen reduction [10] and hydrogen oxidation [9], they have not been tried in methanol oxidation.

Pb-modified Pt electrodes (mostly of the Pb UPD type [11–15] but also of the Pt–Pb alloy kind [16]) have long been tested as anodes but the modification was found to have only a

^{*} Corresponding author. Tel.: +30 2310 997742; fax: +30 2310 443922. *E-mail addresses:* eczss@chem.auth.gr, eczss@otenet.gr (S. Sotiropoulos).

small effect in Pt electrocatalytic activity towards methanol oxidation. This is because Pb cannot provide adsorbed oxygenated species for methanol oxidation [13], a disadvantage that offsets its "third-body effect" (intercepting the Pt sites arrangement needed for poison adsorption [17]).

The aim of this work has been to prepare platinized lead, Pt(Pb), deposits on glassy carbon (GC) supports and (as a control system) on Pt substrates too and test their electrocatalytic activity for methanol oxidation. Specific objectives have been: (i) The microscopic characterisation of Pt(Pb) deposits prepared by surface replacement of pre-deposited thick Pb layers on GC and Pt. (ii) The electrochemical characterisation of the resulting Pt(Pb)/GC and Pt(Pb)/Pt electrodes by means of typical electrochemical reactions (hydrogen adsorption/desorption, hydrazine and formic acid oxidation). (iii) The evaluation of these electrodes as methanol oxidation anodes, by means of voltammetry and constant potential amperometry, investigating the effect of Pb on the catalytic properties of the Pt overlayer.

2. Experimental

2.1. Pb/GC, Pt(Pb)/GC, Pb/Pt and Pt(Pb)/Pt coatings

Electrodeposition of Pb on GC and Pt was carried out from 0.1 M HClO₄ + 0.01 M PbCO₃ deaerated solutions in the mass transfer control region (typically -0.55 V versus Ag/AgCl) as established by preliminary deposition voltammetry. The total charge density passed was 187 mC cm^{-2} , corresponding to the equivalent of 950 flat Pb monolayers (taking the atomic radius of Pb as 0.175 nm and assuming the FCC crystal structure for the Pb deposit [18]). Initial experiments established that, due to deposit non-uniformity, this was the minimum quantity of deposited Pb on GC that was required for eventual clear Pt surface electrochemistry (unaffected by the substrate) and significant methanol oxidation rates.

In this way, the amount of Pb deposited on GC has been controlled by the charge that passed during lead electrodeposition under constant potential; this charge corresponds to ca. 0.19 mg cm^{-2} , based on Faradays law and assuming a 100% current efficiency (preliminary gravimetric experiments confirmed current efficiencies higher than 96%).

Pb/GC and Pb/Pt electrodes were subsequently immersed in a 0.1 M HCl+ 10^{-3} M K₂PtCl₆ solution for 15 min so that spontaneous Pb replacement by Pt occurred:

$$2Pb/GC + PtCl_6^{2-} \rightarrow Pt(Pb)/GC + 2Pb^{2+} + 6Cl^{-}$$
(1)

The Pt(Pb) deposits were etched off from the Pt(Pb)/GC electrodes by immersion in a known volume (5 ml) of aquea regia and the solution was analysed by AA; Pt loadings in the $3-5 \ \mu g \ cm^{-2}$ range were found from a series of experiments and these very low values are indicative of a very thin Pt skin.

2.2. Electrochemical characterisation of coatings

Voltammetric and constant potential deposition or chronoamperometry experiments were carried out with the Autolab 100 (EcoChimie) system, in small three-compartment cells equipped with a luggin capillary at the end of the reference electrode (Ag/AgCl in 3 M NaCl, BAS Inc.; measured as $-0.040 V \pm 5 \text{ mV}$ versus SCE, i.e. $+0.202 V \pm 5 \text{ mV}$ versus SHE) chamber. A Pt coil served as the counter electrode, placed in a compartment separated from that of the working electrode by a glass frit. Three cells were used: one for Pb deposition, one for preliminary Pt(Pb)/GC or Pt(Pb)/Pt activation-cleaning in acid and one for studying Pt surface electrochemistry in acid and methanol oxidation.

Following Pb deposition and immersion into the chloroplatinic acid exchange solution, as prepared Pt(Pb)/GC or Pt(Pb)/Pt electrodes were scanned repeatedly (typically, more than 120 times) at 1 V s^{-1} in the "cleaning" 0.1 M HClO_4 solution between hydrogen and oxygen evolution, ensuring that any unreacted surface Pb was anodically dissolved during exposure to positive potentials. The electrode was then transferred to a clean deaerated 0.1 M HClO₄ solution and scanned again for another 120 times until a steady state picture, typical of Pt surface electrochemistry, was obtained. Finally, the solution was replaced by the working 0.5 M MeOH + 0.1 M HClO₄ deaerated solution and the potential was swept at 5 mV s^{-1} between +0.1 and +0.8 V for three times. Since the voltammetric picture of the second and third run was similar, voltammograms presented here correspond to the second run, deemed as representative of short-term behaviour. Constant potential experiments lasting 300s were performed to obtain an estimate of medium-term catalytic activity towards methanol oxidation. Before the application of the potential of interest all electrodes were subjected to the same potential pulse protocol to ensure similar starting conditions: they were brought in contact with the solution at -0.25 V versus Ag/AgCl for 2s (just prior to hydrogen evolution, where methanol oxidation is minimum), then stepped to +0.55 V versus Ag/AgCl for 2s (for oxidative desorption of adsorbed H during the previous step and facile oxidation of CO formed by methanol oxidation at this potential) and finally stepped to 0.05 V for 2 s (double layer region); they were then stepped to the potential of interest (+0.3, +0.4 and +0.5 V versus Ag/AgCl) for 300 s.

2.3. Electrode materials and chemicals

Glassy carbon from Alfa Aesar (1 mm thick) was cut into 3 mm diameter discs and sealed into glass tubes with epoxyresin glue. A Pt disc electrode (1.5 mm diameter) from BAS Inc. was used as an alternative substrate. Electrodes to be used for SEM/EDS experiments were prepared by connecting the carbon disc or a piece of a Pt foil (Alfa Aesar) to a glass tube via a bridge made of a shrinkable thermoplastic tube. The latter was filled with mercury to ensure electrical contact between the disc and a commercial wire inserted from the open end of the glass tube. In the few indicative experiments of hydrazine oxidation, a glassy carbon (3 mm diameter) RDE controlled by a Taccusel EDI101T motor was used as the substrate electrode.

HClO₄ from Riedel (puriss p.a., ACS reagent, \geq 70%) and PbCO₃ from Sigma–Aldrich (ACS reagent) were used in the preparation of Pb deposition solutions. H₂PtCl₆ hexahydrate from Sigma–Aldrich (ACS reagent, \geq 37.50% as Pt)

was employed for the Pt exchange solution. MeOH was from Riedel (Chromasolv[®], for HPLC, gradient grade, \geq 99.9%). Hydrazinium sulphate pro analysi was from Merck and Formic acid 98–100%, Analytical Reagent, Reag. ACS, Reag. Ph.Eur. was from Riedel-de Haen.

3. Results and discussion

3.1. Microscopic characterisation of Pb and Pt(Pb) deposits

Fig. 1(A) and (B) shows SEM micrographs of a Pb deposit formed by the electrodeposition of 187 mC cm^{-2} (corresponding to ca. 0.19 mg cm⁻² of Pb, see Section 2) onto GC in the

mass transfer control potential range. A thick and dense particulate deposit can be seen which, upon closer inspection reveals the existence of large pyramidal particles (rather monodisperse, $1-2 \,\mu$ m in size), sub-micron nuclei (polydisperse) that coalesce at locations and a few sub-micron needles.

Fig. 1(C) and (D) shows SEM micrographs of the Pt(Pb) deposits resulting from the immersion of the Pb/GC electrodes into the chloroplatinic acid exchange solution and the subsequent potential cycling in acid. It can be seen that the deposit is now sparser (with distinct uncovered GC spots, confirmed by EDS) and thinner, made up of smaller (<1 μ m) and more rounded polyhedra particles as well as isolated nano-sized nuclei. EDS analysis confirmed the existence of Pt in all deposit locations. Results from the electrode area depicted in Fig. 1(C), showed rel-



Fig. 1. SEM micrographs of (A) and (B) electrodeposited Pb on GC (at -0.55 V vs. Ag/AgCl; total charge density 187 mC cm⁻², equivalent of 950 Pb monolayers) and (C) and (D) Pt(Pb) prepared by electroless platinization of the deposits of (A) and (B) (15 min immersion in a 0.1 M HCl + 10^{-3} M K₂PtCl₆ solution). SEM micrographs of (E) and (F) show Pt(Pb) deposits prepared as those of (A) and (D) on Pt.

ative Pt and Pb precentage composition of 72.62% and 27.38%, respectively (it should be stressed that EDS analysis only provides some information on the composition of the deposit layer since it is neither a surface sensitive tool, such as XPS or AES, or can provide a depth profile). The reduction in particle number and size is mainly due to the competition of Pb dissolution in the acid solution and its exchange by Pt which protects the underlying Pb. Once a protective Pt surface layer is formed, the Pb particles are stabilised and no further dissolution takes place (the further reduction in size of very small features such as the needles of Fig. 1(B), results in their collapse). Exposure to positive potentials during potential cycling had a relatively small effect, mainly on particle number, as confirmed by SEM.

Although the main aim of this work has been the study of Pt(Pb) onto a carbon material support (GC), to exclude any possible GC substrate effects, we prepared similar (187 mC cm^{-2}) of initial Pb) deposits on a Pt electrode substrate. Fig. 1(E) and (F) shows Pt(Pb) deposits formed by the two-step technique on Pt. In contrast to Fig. 1(C), Fig. 1(E) shows an almost complete coverage of the surface by a skin of coalescent Pt(Pb) nuclei (confirmed by the presence of Pb at all locations by means of EDS), on top of which larger particles lie. A close comparison of Fig. 1(D) and (F) reveals that the large Pt(Pb) particles on Pt are smaller (less than 1 µm in diameter) than those on GC. The complete coverage of the Pt surface by the Pt(Pb) deposit may be attributed to smaller Pb particle size which permits their fast and complete coverage/protection by Pt before leaching of Pb occurs, as well as to better adherence to the substrate.

3.2. Electrochemical characterisation of Pt(Pb)/GC and Pt(Pb)/Pt electrodes

3.2.1. Surface electrochemistry in acid

Fig. 2(A) shows fast potential sweep voltammograms (at 1 V s^{-1}) recorded in a deaerated 0.1 M HClO₄ solution at a Pt(Pb)/GC and the GC electrode substrate; Fig. 2(B) shows, similar voltammograms at a bulk Pt disc and at a Pt(Pb)/Pt disc electrode. The characteristic features of Pt surface electrochemistry (hydrogen adsorption/desorption peaks and oxide formation/stripping wave/peak) are clearly observed at the Pt(Pb)/GC electrode, indicating that full platinization of the surface of the Pb particles has been achieved and that the contribution of uncovered areas of the GC substrate did not obscure to any significant extent the voltammetric picture. (Note that the higher double layer currents and an oxidative "hump" recorded for the Pt(Pb)/GC should be attributed to GC due to the higher carbon capacitance and surface group electrochemistry [19,20]—see also the voltammogram for GC in the same figure.) The clearly resolved hydrogen adsorption/desorption region permitted an estimate of Pt electroactive surface area, $A_{\rm e}$, as calculated from the corresponding cathodic charge over the capacitive current and the charge associated to the formation or stripping of a H monolayer (210 μ C cm⁻² [21]). This can be quantified by a "roughness factor" $r = A_e/A_{gs}$ where A_{gs} is the substrate geometric area. Electrodes with r values in the 1.2-2 range were obtained; the one depicted in Fig. 2(A) had a



Fig. 2. (A) Voltammograms (at 1 V s^{-1} potential scan rate) of a Pt(Pb)/GC (r=1.3) and the GC substrate electrode, in a deaerated 0.1 M HClO₄ solution. (B) Same as in (A) but for a Pt(Pb)/Pt (r=6.8) electrode and a bulk Pt disc (r=1.0) electrode.

value of 1.3 whereas the polished Pt disc of Fig. 2(B) had r = 1.0. This relatively small electroactive area indicates that incomplete coverage offsets the particulate form of the deposit. To the contrary, the surface electrochemistry of Pt(Pb)/Pt electrodes (see for example Fig. 2(B)) shows a perfectly flat double layer region and, from the hydrogen adsorption charge, r values in the 5–7 range were obtained in line with the higher surface coverage on Pt (confirmed by the SEM micrographs of the previous section).

3.2.2. Hydrazine and formic acid oxidation

Despite the fact that any defective Pt shell–Pb core particles should have dissolved away during the excursion into the anodic potentials included in the pre-treatment voltammetry, the possibility that some additional Pb might dissolve during methanol oxidation experiments and re-deposit as a UPD layer on the Pt skin, does not seem remote at first glance. The clear picture of Pt surface electrochemistry obtained at the Pt(Pb) electrodes (Fig. 2(A) and (B)) is a first evidence against this possibility since it can be contrasted to the distortion caused by even fractions of a Pb UPD, formed at Pb(II) concentrations as low as 10^{-6} M [11]. Nevertheless, to completely exclude such an effect we have also studied two typical electrochemical reactions for Pt electrodes: hydrazine oxidation which is strongly hindered by the presence of Pb UPD [22] and formic acid oxidation which is significantly enhanced by Pb UPD [23–27].



Fig. 3. Voltammograms (at 10 mV s^{-1} potential scan rate) of a Pt(Pb)/GC RDE and a bulk Pt RDE in a deaerated 0.001 M hydrazine + 0.1 M HClO₄ solution, at a 500 rpm rotation rate. Current density is per substrate geometric area.

Fig. 3 presents slow potential sweep voltammograms (at 10 mV s^{-1}) in a 0.001 M hydrazine + 0.1 M HClO₄ solution at a RDE (500 rpm) Pt(Pb)/GC and, for comparison, at a bulk Pt RDE (500 rpm). It can readily be seen that the half-wave potentials of the two voltammograms are similar and no noticeable shift to more positive potentials (characteristic of the presence of Pb UPD [22]) is observed. Furthermore, the limiting current densities for hydrazine oxidation at the Pt and Pt(Pb)/GC electrodes are similar, indicating a complete overlapping of the diffusion fields of the Pt(Pb) particles formed on the GC electrode, resulting in a coincidence of the planar diffusion field cross-section with the electrode geometric area (the current "well" observed in the limiting current region has been observed before at RDEs and attributed to adsorption/desorption of impurities, e.g. chloride ion traces, in the double layer region [22]).

Fig. 4 presents slow potential sweep voltammograms (at 10 mV s^{-1}) in a 0.2 M formic acid + 0.1 M HClO₄ solution at a stationary Pt(Pb)/GC electrode in the presence and absence of Pb(II) in the solution. The Inset shows a similar voltammogram in the absence of Pb(II) for a bulk Pt electrode. The voltam-



Fig. 4. Cyclic voltammograms (at 50 mV s⁻¹ potential scan rate) of a Pt(Pb)/GC electrode in a deaerated 0.2 M formic acid + 0.1 M HClO₄ solution, in the presence and absence of 0.001 M Pb(II), as indicated on the graph. Inset: same as in the main graph but for a bulk Pt disk electrode in the absence of 0.001 M Pb(II). Current density is per substrate geometric area.



Fig. 5. Voltammograms (second positive-going scan at 5 mV s⁻¹ potential scan rate) of a Pt(Pb)/GC (r=1.3), a Pt(Pb)/Pt (r=6.8) and a bulk Pt disk (r=1.0) electrode in a deaerated 0.5 M MeOH + 0.1 M HClO₄ solution. Current density is per substrate geometric area.

metric picture at the Pt(Pb)/GC in the absence of deliberately added Pb(II) is qualitatively the same with that of bulk Pt, with a strongly hindered oxidation process during the positive-going scan (consisting of two waves, whose relative height depends on impurities, potential limits, Pt crystalline form, etc.) and a more facile oxidation during the reverse scan [23–27]. To the contrary, the presence of Pb(II) ions in the solutions that leads to the formation of a Pb UPD in the region of formic acid oxidation, strongly catalyses the process resulting in much higher currents and a smaller hysterisis between the forward and reverse peaks.

In conclusion, the electrochemical characterisation of our Pt(Pb) electrodes presented in Sections 3.2.1 and 3.2.2 confirms the complete coverage of the Pb particles by a protective Pt skin and the lack of any Pb anodic dissolution at potentials relevant to organics oxidation.

3.3. Methanol oxidation in acid

Fig. 5 presents slow potential sweep voltammograms (at 5 mV s^{-1} ; positive going scan) in a 0.5 M MeOH + 0.1 M HClO₄ solution at a Pt(Pb)/GC, a Pt(Pb)/Pt and, for comparison, at a bulk Pt disc electrode (the ones corresponding to the surface voltammetry of Fig. 2).

First of all, it is seen that the peak of methanol oxidation appears at the same potential for all electrodes. It has been welldocumented [11–16] that this peak results from an increase in the current as the potential becomes positive enough for high rates of methanol oxidation to occur (and the poisonous CO intermediate to be oxidized-removed), followed by a current fall beyond that peak as full coverage of the Pt layer with surface oxides and a decrease in the number of catalytic sites take place. Since the oxidative removal of CO at high potentials is not expected to depend on electrode catalytic activity and the potential region of Pt oxide formation does not seem to depend either on whether Pt(Pb) or Pt is used (see surface electrochemistry in Fig. 2(A) and (B)), this peak should appear at the same potential for all electrodes. Table 1

Current densities per electroactive Pt area, *i*_e, at three applied potential values, for methanol electrooxidation at Pt(Pb)/GC, Pt(Pb)/Pt and Pt electrodes, during voltammetric and chronoamperometric experiments in 0.5 M MeOH + 0.1 M HClO₄

	+0.3 V vs. Ag/AgCl	+0.4 V vs. Ag/AgCl	+0.5 V vs. Ag/AgCl
$\overline{i_{\rm e}}$ (µA cm ⁻²) from voltammetry a	t 5 mV s ⁻¹		
Pt (Pb)/GC ($r = 1.3$)	14	192	609
Pt(Pb)/Pt (r = 6.8)	24	243	722
Pt $(r = 1.0)$	8	111	391
$i_{\rm e}$ (μ A cm ⁻²) after 300 s at constant	nt potential		
Pt (Pb)/GC ($r = 1.7$)	21	61	149
Pt(Pb)/Pt (r = 5.5)	55	123	249
Pt $(r = 1.0)$	0	1	140

Second, and most important, it is seen that the platinized lead electrodes exhibit higher currents per substrate geometric area than the surface area increase would explain. This is confirmed by the results of Table 1 where the current densities per electroactive area are tabulated for the three electrodes and for three indicative potentials of +0.3, +0.4 V (foot of the wave) and +0.5 V (close to the peak of the wave). Thus, an enhanced catalytic activity of the Pt(Pb)-modified electrodes towards methanol electrooxidation is already suggested by voltammetry. However, with respect to the prospective use of such catalysts in direct methanol fuel cells and in connection with their performance deterioration with time due to electrode poisoning, it is well-established that catalysts for methanol electrooxidation should be evaluated under constant potential conditions [28–30]. Fig. 6 shows the current-time response following a potential step to +0.4 V versus Ag/AgCl at a Pt(Pb)/GC, a Pt(Pb)/Pt electrode and a bulk Pt disc, in a solution of 0.5 M MeOH + 0.1 M HClO₄. It is seen that, apart from the fact that the current density is higher at the Pt(Pb)-modified electrodes (as it is also the case for the corresponding current densities per electroactive Pt area—see Table 1 again), the signal at the latter is falling at a much smaller rate than that at the pure Pt electrode (similar extremely low currents have been reported after long periods for pure Pt in [28] too), indicating a diminished contamination rate at the modified electrodes. This is further supported by noting in Table 1 that methanol oxidation currents after 300 s are more enhanced at



Fig. 6. Chronoamperometric curves following the application of +0.4 V vs. Ag/AgCl at Pt(Pb)/GC (r=1.7), Pt(Pb)/Pt (r=5.5) and bulk Pt disk (r=1.0) electrodes in a dearated 0.5 M MeOH + 0.1 M HClO₄ solution. Current density is per substrate geometric area.

+0.3 and +0.4 V for Pt(Pb) electrodes (where the poison oxidation rates are expected to be low) than at the higher potential of +0.5 V (where the oxidative removal of the poison is expected to be more efficient).

A comparison of our results with those of the seminal works of Refs. [28,29] for smooth Pt-Ru electrodes (the state-of-art material for methanol anodes), reveals that the current densities obtained at our Pt(Pb) electrodes after 300 s at +0.3 V versus Ag/AgCl, 3 M NaCl (i.e. at ca. +0.5 V versus SHE) in a 0.5 M MeOH solution are, depending on electrode, in the $21-55 \,\mu\text{A}\,\text{cm}^{-2}$ range (Table 1) i.e. in the lower end of the $30-200 \,\mu\text{A}\,\text{cm}^{-2}$ range (depending on Ru content) reported under similar conditions in [28,29]. Nevertheless, the advantage of our electrodes lies on the fact that Pt modification is based on a cheap Pb substrate rather than on an expensive Ru second metal component. At this point we would like to stress that the reason our results should be compared with those of [28,29] is two-fold: first, the potential and methanol concentration conditions are identical to ours; second, and more importantly, Pt-Ru electrodes used therein were smooth, unsupported electrodes, a situation more similar to our large particle and low roughness factor (ca. 1.2–7) Pt(Pb) electrodes than that of commercial precious metal/carbon powder catalysts. Finally, we should also point out that potentials as high as +0.5 V versus SHE (+0.3 V versus Ag/AgCl) have been used in basic research studies utilising smooth electrodes to characterise the catalytic activity of materials towards methanol oxidation (as in this work and [28,29]). This is because current densities (especially during long term experiments) at smooth electrodes are very small (and thus prone to errors) as opposed to the situation of high surface area real catalyst electrodes (which are usually evaluated at lower potentials [30]).

The increased tolerance of Pt(Pb) electrodes to poisoning during methanol oxidation at first sight contradicts the generally accepted view that Pb has a very small effect on MeOH oxidation at Pt as an adatom [11–15] (see also the discussion in Section 1). However, molecular orbital calculations have predicted that a "ligand effect" of Pb (and Sn) on Pt should be present too, promoting CO desorption from Pt [31]. This electronic-"ligand" effect of Pb on Pt should be the only effect operative when a Pb underlayer is fully coated with Pt, hence it could be responsible for the high catalytic activity and medium term stability of Pt(Pb) electrodes towards methanol oxidation.

- (i) Adherent platinized lead deposits with particle size in the few microns and sub-micron ranges, have been prepared on glassy carbon and platinum substrates by a two-step process that involves lead electrodeposition and spontaneous platinum deposition on lead from its chloro-complex solutions.
- (ii) The prepared Pt(Pb)/GC and Pt(Pb)/Pt electrodes exhibited higher catalytic activity and stability towards methanol electrooxidation than bulk Pt. The enhancement of the catalytic activity of Pt is attributed to an electronic effect of the Pb underlayer on the Pt surface layer, affecting the extent of poison adsorption on the latter.
- (iii) This two-step method for catalyst preparation opens up new opportunities for low precious catalyst loadings, limited to a thin surface layer on top of less expensive metal particles. However the focus of this paper has been the study of the catalytic effect of the Pb underlayer on the Pt skin, and not the preparation of a practical catalyst at this stage; that would require the precursor Pb particles to be much smaller, prepared for example by a chemical method or a pulse deposition technique.
- (iv) This method allows the study of the electronic effect alone of the second component underlayer to the precious metal overlayer. It thus offers the possibility to distinguish between the bi-functional and electronic effect mechanisms for a variety of other bi-metallic catalysts, by comparing the behaviour of surface alloys or UPD-modified electrodes with electrodes produced by the electrodeposition/electroless deposition technique.

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