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The promotion of CO electro-oxidation on platinum–bismuth as a model for surface mediated oxygen transfer

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Abstract

The results of electrochemical studies of CO oxidation on clean and bismuth modified Pt(1 1 0)-(1×2) and Pt(1 1 1) surfaces and a supported platinum catalyst are compared. The effect of sub-monolayers of bismuth is to increase the CO oxidation potential on Pt(1 1 0)-(1×2), and decrease it on Pt(1 1 1). This primarily reflects the rather low potential for CO oxidation characteristic of the more open packed Pt(1 1 0)-(1×2) surface, and the higher potential characteristic of the close packed Pt(1 1 1) face. The oxidation potential of CO in the intermixed CO/Bi phases on the single crystals is very similar. The effect of bismuth on the supported platinum catalyst is to increase the CO oxidation potential by a similar amount to that found for Pt(1 1 0)-(1×2). In addition, modification by bismuth results in a concomitant reduction in the CO tolerance of the commercial catalyst. CO oxidation on the catalyst exhibits poisoning by bismuth in a similar fashion to Pt(1 1 0)-(1×2), and the bismuth redox couple on the catalyst is the same as that found on Pt(1 1 0)-(1×2). High coverages of bismuth on the catalyst do not appear to reduce its activity for hydrogen oxidation. These results are discussed in the context of the requirement for surface mediated oxygen transfer during CO electro-oxidation. © 1997 Elsevier Science B.V.

Keywords: Catalysis; Fuel cell; Electro-oxidation; Platinum; Bismuth; Carbon monoxide; Hydrogen

1. Introduction

Despite some 40 years of research and development, platinum based catalysts remain the most active available for the electro-oxidation of hydrogen and methanol at the anodes of the SPFC and DMFC, respectively [1]. At working potential the surface responsible for the catalytic activity is believed to be clean metallic platinum, usually highly dispersed as metal particles on a carbon support. Platinum, as a catalyst for electro-oxidation, is susceptible to poisoning by CO, which is known to irreversibly chemisorb on platinum under anodic conditions. In the SPFC the source of CO is directly from the hydrogen feed, particularly when the latter is supplied from reformed methanol. In the case of the DMFC, a competing branch of the electro-oxidation of methanol is believed to produce adsorbed CO as a poisoning intermediate [2]. On-line removal of CO from the hydrogen feed is both complicated and expensive, particularly for SPFC automotive applications. The preferred option is therefore to improve the CO tolerance of the anode catalyst, primarily through the promotion of CO electro-oxidation resulting in a facile desorption of CO_2 from the platinum, freeing active sites for hydrogen oxidation. A similar promotion may

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also be the solution to self-poisoning in the DMFC, although modifications resulting in selective oxidation channels may be an alternative. The promotion of platinum catalysts by a second metal component at the surface is an important route to CO tolerant fuel cell anodes.

The role of the promoter in CO electro-oxidation is to reduce the ca. 0.8 V over-potential for the process on platinum. This over-potential has been shown to be sensitive to a number of factors such as CO coverage [3], the order of the CO overlayer [4,5], the presence of co-adsorbed anions [6], the structure of the surface [5,7] and the presence of CO in the bulk electrolyte [8]. Understanding the origin of the over-potential, and any significant reduction induced by a metal promoter, requires an understanding of the mechanism and rate limiting (and perhaps activated) step(s) determining the dynamics and kinetics of the oxidation process. Promotion could be achieved by modifying the CO platinum interaction in order to enhance oxidative removal, or it may increase the rate by enhancing the availability of reactive oxygen at the surface at anodic potentials. Ruthenium is most commonly used as the promoter in SPFC and DMFC applications, and the enhancement of CO oxidation at lowered potential has been associated with both a perturbation of the adsorbed CO [9] and the promotion of oxygen transfer [10]. Incorporation and alloying of ruthenium in platinum, and the facile oxidative dissolution of ruthenium from the surface makes fundamental studies of this promotion particularly difficult in MVD transfer studies [11], although a series of experiments has been carried out on single crystal alloy surfaces [12]. Bismuth has recently provided a more accessible model for the study of the promotion of CO oxidation on platinum [5]. It can be adsorbed from solution, and is stable over a significantly large window of potential to allow the study of its influence on CO electro-oxidation. Bismuth has traditionally been considered a purely third body (ensemble) type modifier which exerts little influence on the electronic structure of the platinum. Similar conclusions have been drawn from surface science studies of bismuth modified single crystal surfaces of platinum [13,14] on which the metal produces a series of well-ordered super-lattices as a function of coverage.

Studies of CO electro-oxidation on a series of bismuth modified single crystal platinum surfaces [5,16,17] are summarised and compared to results obtained by modifying a commercial platinum based gas diffusion catalyst for the SPFC [15]. The results highlight the importance of the platinum surface structure in determining the effectiveness of bismuth as a promoter. Further, the modification associated with the bismuth is understandable in terms of its ability to mediate oxygen transfer at the surface.

2. Experimental

Experiments have been performed on the Pt(1 1 0) single crystal surface using the UHV-electrochemical transfer system described in detail elsewhere [5]. Pt(1 1 0) was prepared in the UHV chamber by Ne^+ bombardment, annealing at 1100 K and a mild oxygen treatment (4×10^{-7} Torr at 575 K) to remove residual carbon. Bismuth adsorption was by MVD, and the coverage of bismuth (defined as the ratio of bismuth atoms to the number of top layer platinum atoms in a (1×1) surface) was established from a combination of LEED on the series of well-ordered overlayer structures [14] and XPS. Surfaces were transferred under controlled conditions to an electrochemical cell which incorporated three electrodes; a hydrogen charged palladium wire was used as a reference, a platinum foil as a counter electrode, and a platinum wire common electrode enabling the cell to be held under potential control at the moment of contact with the sample working electrode. The supporting electrolyte was 0.5 M H_2SO_4 (Aldrich 5 N), and 1×10^{-3} M Bi^{3+} solutions prepared from Bi_2O_3. Cyclic voltammetry was performed using a HI-TEK PPR1 potentiostat at a scan rate of 100 mV s^{-1}. All potentials are quoted with reference to Pd/H_2 (+0.05 V vs. RHE).

The studies on the carbon supported platinum catalyst were carried out on a gas diffusion electrode with a loading of 0.22 mg Pt cm^{-2} supplied by Johnson Matthey. A full description of the cells allowing cyclic voltammetric and polarography will appear elsewhere [15]. A disc of the electrode was prepared by soaking for 10 min in iso-propyl alcohol, rinsing and boiling for 30 min in water to remove any remaining alcohol, and subsequently soaked in 1 M H_2SO_4 for 5 min. This produces a "flooded" electrode which was characterised by performing CO oxidations with and without the presence of bismuth. Bismuth was dosed from a 1 M H_2SO_4 solution saturated with Bi^{3+} nominally 0.02 M and adsorption of CO was carried out by passing the gas over the working electrode whilst the electrode was held at 5 mV before purging with nitrogen for 15 min. Data acquisition was performed using a Sycopel Scientific 703C/736 potentiostat driven by an IBM compatible PC. All cyclic voltammograms (CV) reported are performed in 1 M H_2SO_4 (BDH Volumetric Solution) at 30 mV s^{-1} and 80°C unless otherwise stated. All potentials are referenced to the Pd/H_2 electrode. In order to study hydrogen oxidation polarisation curves on the characterised flooded electrodes, they were dried and coated with a proton exchange membrane (Nafion-Solution Technologies) so as to allow operation as gas diffusion electrodes. Polarisation curves were measured on clean and bismuth modified electrodes for pure hydrogen and CO/hydrogen feeds at 80°C, and are *iR* corrected (using a current interrupt method under hydrogen oxidation conditions).

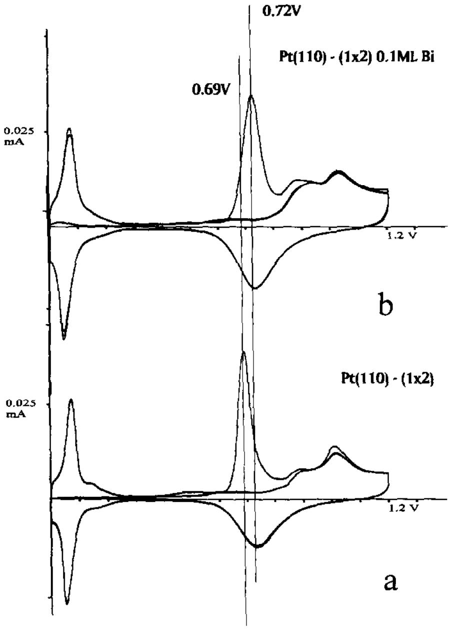

Fig. 1. A cyclic voltammogram showing the electro-oxidation of a saturated CO overlayer adsorbed on (a) the clean and (b) bismuth modified (0.1 ML Bi) Pt(1 1 0)-(1×2) surface.

3. Results and discussion

3.1. Electro-oxidation of carbon monoxide on Pt(1 1 0)

Fig. 1(a) shows the CV characteristic of the first two cycles after the pre-adsorption of CO on Pt(1 1 0)-(1×2). In these experiments, following transfer of the surface, contact is first made with sulphuric acid electrolyte at 0.4 V. Following characterisation of the clean surface by voltammetry [5], contact is broken and re-made with the CO containing solution under potential control. Subsequent CO electro-oxidation is carried out in a CO free electrolyte. The first cycle shows a strong peak at 0.69 V which can be associated with the electro-oxidation of the adsorbed CO. Complete oxidation is confirmed by the return to the standard Pt(1 1 0) trace [5] in both the hydrogen and oxygen regions on the second cycle. A CO layer adsorbed from solution under potential control at 0.4 V was transferred back into UHV. TPD of the overlayer produced the doublet structure characteristic [18] of the saturated CO(2×1)p1g1 overlayer. This is in agreement with the conclusions of others [19]. We have therefore assumed that the charge associated with the CO oxidation in Fig. 1a corresponds to the oxidation of 1 ML of CO.

The effect of bismuth pre-adsorption on the subsequent adsorption and electro-oxidation of CO on the Pt(1 1 0)-(1×2) surface is shown in Figs. 1–3 together with the result on the clean surface for comparison. Bismuth has been deposited on the Pt(1 1 0)-(1×2) surface by MVD in the UHV chamber under conditions which allow the formation of a number of well-ordered overlayers which are characterised by LEED and XPS [14]. Co-adsorption of CO with bismuth reveals that mixed adlayers of bismuth and CO are formed over a wide coverage range, with little perturbation of the CO bonding to the platinum. A simple linear blocking of sites for CO adsorption with bismuth coverage is observed both at the UHV [14] and electrochemical interface [5]. Fig. 4 is a model of one of the suggested mixed CO/Bi structures observed on Pt(1 1 0)-(1×2) on the basis of the LEED, XPS and CO TPD results. The bismuth coverage is 0.25, and the CO coverage is 0.5.

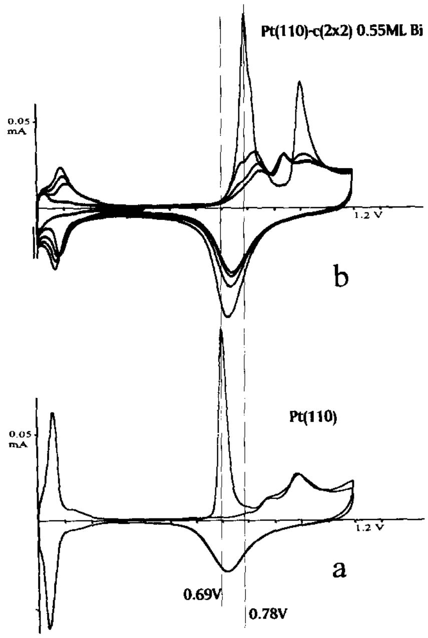

Fig. 2. A cyclic voltammogram showing the electro-oxidation of a saturated CO overlayer adsorbed on (a) the clean and (b) bismuth modified (0.55 ML Bi) Pt(1 1 0)-(1×2) surface.

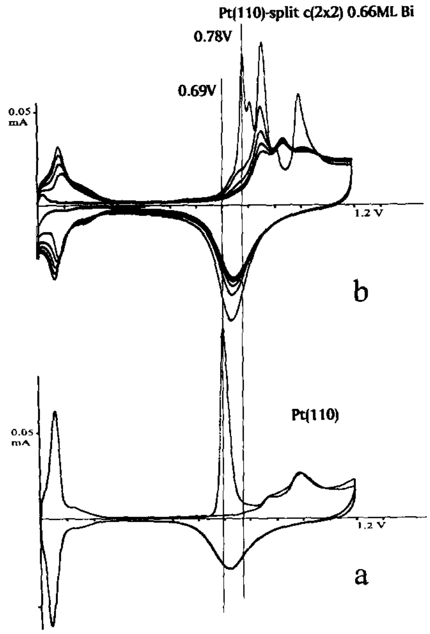

Fig. 3. A cyclic voltammogram showing the electro-oxidation of a saturated CO overlayer adsorbed on (a) the clean and (b) bismuth modified (0.66 ML Bi) Pt(1 1 0)-(1×2) surface.

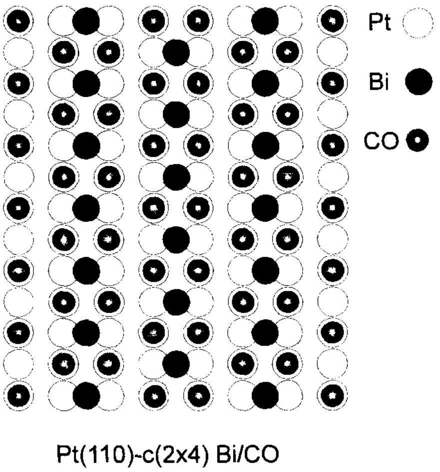

Fig. 4. A real space model for the c(2×4) co-adsorbate structure of CO and Bi on Pt(1 1 0)-(1×2) [14]. The bismuth coverage is 0.25 ML, and the CO coverage is 0.5 ML.

Results are presented in Figs. 1–3 for three bismuth coverages. CO is adsorbed at 300 K under UHV conditions, the surface is subsequently transferred to the ECC, contact made under potential control at 0.4 V, and then cycled first to 0 V to check integrity of the overlayer through its modification of the hydrogen UPD region. A series of oxidation cycles is then carried out in order to investigate the CO oxidation. Fig. 1b shows CO oxidation Pt(1 1 0)-(1×2)Bi 0.1 ML surface. Comparison with the electro-oxidation on the clean surface (Fig. 1a) reveals that from the lowest bismuth coverage studied, the presence of bismuth clearly modifies the electro-oxidation behaviour of CO. At a coverage of 0.1 ML of bismuth, the CO oxidation peak has shifted to 0.72 V from the clean surface value of 0.69. Note also that the peak has broadened significantly, with an onset similar to that of the clean surface. At this coverage, the bismuth has not yet fully lifted the (1×2) surface reconstruction, but there are intermixed regions of bismuth and CO which form complete ordered structures at a slightly higher coverage of 0.25 ML of bismuth [14]. The effect of the bismuth is to increase the oxidation potential of the CO in these intermixed layers, and the broadening is a result of the heterogeneous nature of the incomplete overlayer which also presents regions of clean Pt(1 1 0)-(1×2) surface. Under these conditions the subsequent oxidation of the bismuth layer after CO has been removed is the same as that characteristic of the clean surface at 0.1 ML of bismuth [5].

The CV showing CO electro-oxidation on the Pt(1 1 0)-c(2×2)Bi at 0.55 ML surface is shown in Fig. 2b. The first cycle differs from subsequent cycles in the observation of two distinct and sharp anodic peaks, the first at 0.78 V with a shoulder at slightly higher potential. The second peak occurs at 1.0 V, which lies well into the region for oxidation of the platinum substrate, has a non-Gaussian shape with a sharp onset, and follows a region which shows an anodic current even below that of the Pt(1 1 0)-(1×2) surface itself. We assign the first peak and shoulder to the electro-oxidation of the CO, at a potential shifted from the clean surface value of 0.69 V, and similar to that found on the low coverage (0.1 ML) bismuth modified surface (Fig. 1b). At a bismuth coverage of 0.55 ML, the co-adsorbed CO layer produces an intermixed phase with retention of the c(2×2) ordered structure characteristic of the bismuth atoms alone [14]. Electro-oxidation in this closely packed mixed phase has shifted to a narrower peak at higher potential which overlaps the normal oxidation potential of bismuth in the absence of CO. We suggest [5] that CO oxidation at this potential is mediated by oxygen associated with the bismuth. Oxygen mediation via. the Pt(1 1 0)-(1×2) surface is hindered by the close packed layer resulting in an onset for CO electro-oxidation which is clearly higher (Fig. 2b) than the clean surface (Fig. 2a). Once the CO has been oxidised and the product desorbs, the resulting bismuth layer is thermodynamically unstable as a result of the depletion of oxygen. The result is a kinetically limited oxidation of the bismuth layer resulting in the second anodic peak at 1.0 V which corresponds to the delayed oxidation of the bismuth. Subsequent cycles show a return to the normal oxidative stripping behaviour of bismuth on Pt(1 1 0)-(1×2) expected at these bismuth coverages [5].

The CV showing CO electro-oxidation on the Pt(1 1 0)-streaked c(2×2)Bi 0.66 ML surface is shown in Fig. 3b. The resulting first sweep in which the CO oxidation takes place is similar to that found at 0.55 ML of bismuth (Fig. 2b) with the exception of an additional peak at 0.85 V, and a more resolved shoulder to the now smaller CO oxidation peak at 0.78 V. At a coverage of 0.66 ML of bismuth, the bismuth layer is undergoing uniaxial compression of the c(2×2) structure, and a very low coverage of CO is now adsorbing (0.2 ML) in a mixed layer [14]. CO is unable to adsorb in regions where the compression is complete, with complete poisoning of CO adsorption at 0.75 ML bismuth. The smaller concentration of CO, reflected in the small CO oxidation peak, results in a smaller peak at 1.0 V over that observed on the 0.5 ML surface (Fig. 2b) since less oxygen has been consumed from the bismuth layer. In addition there are now regions of bismuth uninfluenced by the competition for available oxygen by CO, and a bismuth oxidation of these less perturbed regions is observed at 0.85 V, close to the normal potential for bismuth oxidation [5]. The small contribution to the anodic current in the shoulder of the CO oxidation peak may also be associated with the oxidation of this less perturbed bismuth (there is a doublet in the high coverage bismuth couple [5]).

Table 1 summarises the potentials found for CO oxidation on the clean and bismuth modified Pt(1 1 0) surface together with results obtained under similar conditions (H_2SO_4 electrolyte, scan rate 50 mV s^{-1}, CO adsorbed from solution and oxidised in CO free electrolyte) on Pt(1 1 1) modified by bismuth adsorbed from solution [16,17]. A cyclic voltammogram showing CO oxidation on a bismuth modified

Table 1

System	Pt(1 1 1)[a] (V)	Pt(1 1 0)-(1×2)(V)	Catalyst (V)
CO oxidation on clean surface	0.82	0.69	0.62
Bismuth redox at $\Theta_{Bi}=0.1$	0.57	0.88	0.88
CO oxidation $\Theta_{Bi}=0.1$	0.72, 0.75	0.72	0.65
CO oxidation $\Theta_{Bi}=0.55–0.66$ (0.65[b])		0.78	0.69

[a] Data for Pt(1 1 1) taken from Ref. [14].
[b] Bismuth coverages on catalyst.

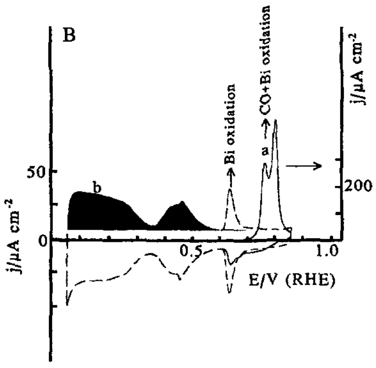

Fig. 5. A cyclic voltammogram showing the electro-oxidation of a saturated CO overlayer (solid curve) adsorbed on the bismuth modified (0.1 ML Bi) Pt(1 1 1) surface, taken from [16]. The dotted curve shows the bismuth oxidation on the clean surface.

(0.1 ML) Pt(1 1 1) surface [16] is shown in Fig. 5. The solid curve shows a contribution of CO oxidation associated with a mixed CO/Bi layer at a potential (0.72 V vs. Pd/H_2) lower than that found for the clean Pt(1 1 1) surface (0.82 vs. Pd/H_2). The clean surface CO oxidation potential at 0.69 V on Pt(1 1 0)-(1×2) is shifted to higher values (0.72–0.78 V) when intermixed in the bismuth overlayer. The clean surface CO oxidation potential on Pt(1 1 1) of 0.82 V is shifted down to the same value (0.72 V) in the intermixed bismuth layer [16,17]. We have suggested [5] that the oxidation of CO on the clean and bismuth modified surfaces is substrate mediated, i.e., the oxidant is first bound to the platinum or bismuth prior to the oxidation of the CO. The differences in CO oxidation potentials (Table 1) therefore reflect the ability to oxidise the free substrate (platinum or bismuth) sites. In the case of the mixed CO/bismuth layers, the different potentials observed on the clean surfaces of Pt(1 1 1) and Pt(1 1 0)-(1×2) for CO (Table 1) are shifted to similar values (0.72–0.78 V) in the presence of bismuth. The result is a promotion of the CO oxidation by bismuth on Pt(1 1 1) [16,17] and a poisoning on Pt(1 1 0)-(1×2) which results from the significantly different potentials for CO oxidation on the clean surfaces. The perturbation of the CO oxidation potential to higher values on Pt(1 1 0)-(1×2) is therefore consistent with a model involving bismuth mediated oxygen transfer. The oxidation of the surface bismuth probably involves the presence of an oxygenated surface species such as $Bi(OH)_2$ or BiO. The requirement for bismuth mediated electro-oxidation has also been suggested recently by Aldaz [16,17]. A corollary of this model is that the CO oxidation on the clean platinum surface also involves substrate mediated oxidation, and that this channel is blocked by high coverages of bismuth adsorbed on Pt(1 1 0)-(1×2).

The relatively facile oxidation of CO on clean Pt(1 1 0)-(1×2) at 0.69 V over Pt(1 1 1) at 0.82 V must therefore also reflect the different oxidation potentials of these surfaces. We do see a small anodic current on Pt(1 1 0)-(1×2) at 0.65 V which we have tentatively ascribed to an oxidation process which may provide a suitable intermediate for CO oxidation [5]. The apparently small amount of charge associated with this process may indicate an oxidation involving defects, or the involvement of a small net charge in an oxidative process in the Pt(1 1 0)-(1×2) unit cell in the presence of exchanging anions. Further evidence that a surface process is taking place at the potentials below the more substantial oxidation above 0.7 V on Pt(1 1 0) without significant net charge transfer comes from electro-reflectance measurements where optical absorption begins to increase for both p and s polarised light at 546 nm above ca. 0.4 V [20]. One may have intuitively predicted that the more open packed face of platinum would promote more effective oxygen transfer, and if critical in CO oxidation one may expect that more open packed sites on supported platinum will also effectively promote electro-oxidation and CO tolerance.

3.2. *Electro-oxidation of carbon monoxide and CO tolerance of Pt catalysts*

Fig. 6 shows the oxidation of carbon monoxide on an unmodified supported platinum electrode (a), and an electrode where the platinum has been modified by adsorbed bismuth (b). Bismuth has been deposited on the electrode by a dipping procedure [15]. The coverage of bismuth is 0.1 ML, a value estimated from the bismuth oxidation charge. Bismuth deposited using this technique has been investigated on both Pt(1 1 1) [21] and Pt(1 1 0) [5] surfaces. Oxidation of CO on the unmodified catalyst takes place in a broad peak centred at 0.62 V. The effect of the pre-adsorbed bismuth is to shift the oxidation potential of CO to higher values. The catalyst modified by a bismuth

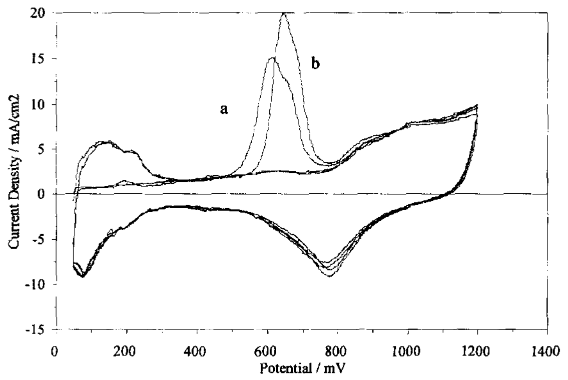

Fig. 6. A cyclic voltammogram showing the electro-oxidation of a saturated CO overlayer on (a) the unmodified platinum catalyst and (b) on the bismuth modified (0.1 ML) catalyst.

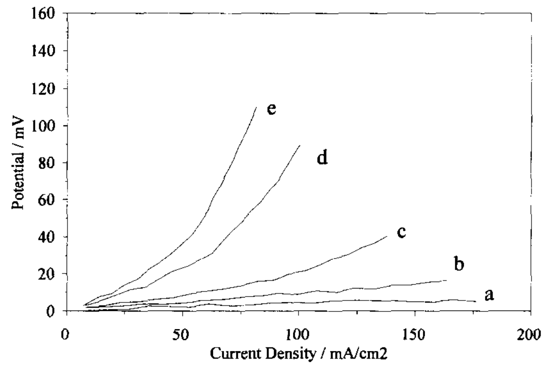

Fig. 7. Hydrogen steady state oxidation polarisation curves from an unmodified supported platinum gas diffusion electrode under conditions of (a) pure H_2, and 100 ppm CO in H_2 for (b) 5 min; (c) 15 min; (d) 30 min; (e) 60 min.

coverage of 0.1 ML exhibits a CO oxidation peak at 0.65 V.

This corresponds to an upward potential shift induced by the bismuth of 0.03 V, a shift similar to that induced by low coverages of bismuth on Pt(1 1 0)-(1×2). Note also that the potential corresponding to the onset of CO oxidation is also significantly perturbed to higher potentials by the adsorbed bismuth (Fig. 6). The redox behaviour of the bismuth adatoms can be just observed at 0.88 V superimposed upon the oxidation/reduction of the platinum crystallites. Increasing the bismuth coverage to 0.65 ML was accompanied by a concomitant increase of the CO oxidation potential to 0.69 V (Table 1). The higher coverage of bismuth was adsorbed by underpotential deposition [5,15]. Table 1 also includes the CO and Bi oxidation potentials (Fig. 6) obtained for the catalyst for comparison with the single crystal results.

Further to the cyclic voltammetric investigations, polarisation studies of the clean and modified supported platinum electrodes were carried out. Both the unmodified and bismuth modified electrodes were investigated [15]. In order to establish the CO tolerance of the electrodes, in addition to experiments involving pure H_2, polarisation curves of the hydrogen oxidation were carried out after exposure to hydrogen feeds at various times containing 100 ppm CO in H_2. Fig. 7 shows the polarisation curves obtained on the unmodified electrode, and Fig. 8 are a series of polarisation curves obtained under identical conditions on an electrode where the platinum has been modified by adsorbing 0.65 ML of bismuth. Under these conditions the peak CO oxidation potential measured in cyclic voltammetry has increased to 0.69 V on the supported platinum surfaces (Table 1).

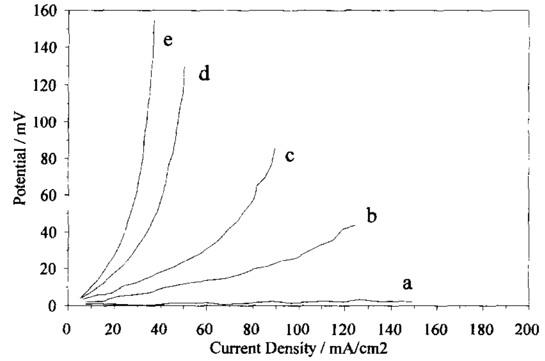

Fig. 8. Hydrogen steady state oxidation polarisation curves from a bismuth modified (0.6 ML) supported platinum gas diffusion electrode under conditions of (a) pure H_2, and 100 ppm CO in H_2 for (b) 5 min; (c) 15 min; (d) 30 min; (e) 60 min.

Two important observations can be made by comparison of the two sets of polarisation curves (Figs. 7 and 8):

(1) There is a linear polarisation response for both the clean and bismuth modified electrodes up to the highest current densities investigated, with identical (within experimental error) and very small overpotential required to obtain high currents. Despite the high

bismuth coverage, therefore, the sites active in the oxidation reaction appear to remain unaffected. Clearly because of the fast kinetics of the oxidation process, one must be careful not to over interpret such a result, but it does appear that the site involved in determining the reaction rate on the platinum is not modified significantly by adsorbed bismuth. The active site in the reaction may or may not be associated with the hydrogen adsorption site which we have noted is not blocked at the same rate on Pt(1 1 0)-(1×2) by bismuth as CO [5]. Previous studies on Pt(1 0 0) [22] have indicated that bismuth does lower the rate of the hydrogen evolution reaction, no strong electronic effect is exerted on the reaction by the bismuth, but that the UPD hydrogen is not involved as a reaction intermediate. This question, however, underlines the fundamental question concerning the reaction kinetics and dynamics responsible for a surface process involving molecular dissociation at metals and alloys where several channels may be operating [23,24]. From a practical point of view it is encouraging in the case of hydrogen platinum electrode surfaces that adsorbate modifications can be made which perturb the rate of CO oxidation without apparently effecting the hydrogen oxidation reaction. Clearly these should be designed to increase CO tolerance rather than reduce it (see later)!

(2) The effect of CO poisoning on the oxidation of the CO on the unmodified catalyst (Fig. 7) is reflected in the increasing overpotential required to obtain the same current density as the time of CO exposure is increased. A modification of the catalyst which resulted in increased CO tolerance would be reflected by a reduction in the overpotential required to obtain the same current density for the same exposure to CO. Fig. 7 shows that for similar conditions of CO exposure (same times of exposure to CO/H_2 mixtures) on the bismuth modified surface, the overpotential is increased, indicating a marked decrease in CO tolerance. This result is consistent with the observed effective poisoning of the CO oxidation reaction as reflected in the increased potential induced by bismuth in the cyclic voltammetry on the supported platinum electrodes (Fig. 6 and Table 1). In the case of 0.6 ML of bismuth, the potential has increased from 0.62 to 0.69 V.

We associate the reduction in CO tolerance on the supported platinum electrodes by the bismuth with the reduced effectiveness of bismuth (over the unmodified surface) to facilitate oxygen transfer during CO oxidation. The unmodified catalyst exhibits CO oxidation (and hence surface mediated oxygen transfer) at potentials similar to the more open packed Pt(1 1 0)-(1×2) surface (Table 1). The effect of bismuth, which mediates oxygen transfer at a higher potential, is therefore to inhibit CO oxidation (as found for Pt(1 1 0)-(1×2)). Note that the absolute values of the CO oxidation on the unmodified and bismuth modified catalyst are all shifted down approx. 0.08 V with respect to the Pt(1 1 0)-(1×2) surface. This may be associated with a temperature dependence in the oxidation kinetics [25]. The changes induced by the bismuth on the catalyst are very similar to those obtained on Pt(1 1 0)-(1×2). The effect of bismuth to promote CO oxidation on Pt(1 1 1) which stems from the higher initial potential of CO oxidation on the clean surface, is therefore quite different from the behaviour of the catalyst.

It appears therefore that the CO oxidation behaviour of the commercial catalyst is quite different from the close packed Pt(1 1 1) surface. Indeed the bismuth redox potential (Table 1) observed on the catalyst and the Pt(1 1 0)-(1×2) surface is similar (0.88 V), while that characteristic of the Pt(1 1 1) surface [16] 0.57 V is quite different.

4. Conclusions

Surface and catalytic studies of single crystal and commercial supported platinum catalysts have provided an insight concerning the factors influencing CO tolerance and hydrogen oxidation activity, and adsorbed metals which influence these processes. Bismuth effectively reduces the CO tolerance of the commercial catalyst by inhibiting surface mediated oxygen transfer during CO electro-oxidation. This is because the unmodified catalyst shows behaviour more similar to the open packed Pt(1 1 0)-(1×2) surface (where bismuth also inhibits CO oxidation) than the Pt(1 1 1) surface (where bismuth promoted oxidation). It also appears that while the effect of the adsorbed bismuth is to strongly perturb the CO tolerance and oxidation behaviour of the catalyst, the activity for hydrogen oxidation in the absence of CO is not changed.

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