The characterization of Pt/Sn catalyst for the electrochemical oxidation of methanol

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Pt/Sn electrodeposited catalysts have been prepared, characterized and tested for the electro-oxidation of methanol. Catalyst activities were measured in 3 M H_2SO_4 electrolyte between ambient temperature and 95° C. Enhancement in specific activity by a factor of about 50 was found over electrodeposited platinum black. This behaviour is in contrast to that of alloys of platinum and tin which were found to have very low activities compared with platinum catalysts and to be readily corroded in H_2SO_4 electrolyte.

ESCA (electron spectroscopy for chemical analysis) studies and Mössbauer spectroscopy showed the majority of the tin in the deposit to be present in an oxidized form. A small amount (~17%) was present as a dilute alloy of tin in platinum. Surface area measurements and X-ray powder diffraction indicated that the increase in activity over platinum black was not attributable to smaller platinum particle size. It seems that the combination of platinum and tin results in a decrease in the poisoning effect by strongly adsorbed organic residues. Whether this arises from the operation of a cyclic Sn(II)/Sn(IV) redox system or from modification of the platinum surface remains unresolved.

1. Introduction

Over the years there has been considerable interest in the use of methanol in a fuel cell. Methanol would be more attractive as fuel than, say, hydrogen since it is much easier to store and handle. However, it is considerably less reactive than hydrogen, and the main obstacle to progress in methanol fuel cells has been the slow development of cheap, active electro-oxidation catalysts.

Electrocatalysts based on metals of the platinum group, and in particular platinum, show significant activity for the anodic oxidation of methanol [1]. However, even on a platinum surface the reaction takes place at an overpotential of about 0·5–0·6 V above the thermodynamic potential (+0·043 V) for the oxidation of methanol to carbon dioxide [2]. Considerable enhancement of the activity of platinum can be obtained by 'alloying' with second metal components, which may modify the adsorption properties of platinum. In this respect the electrocatalysts can be compared with some gas-phase dehydrogenation catalysts. The term 'alloying'

does not necessarily imply true alloying, but rather the intimate mixing of two metal components, e.g., Pt/Ru, Pt/Re and Pt/Sn combinations [3, 4] have been shown to have considerably enhanced activity over platinum, and in no case has true alloying been shown to be a pre-requisite for the high activity.

A recent paper by Cathro [4] showed that electrodeposits of Pt/Sn have activities at least two orders of magnitude higher than has electrodeposited platinum black in H_2SO_4 electrolyte. A suggested function of the tin was proposed, namely that tin was present in the catalyst in an oxidized form and functioned in a redox manner. Normally, on platinum catalysts, the electro-oxidation of methanol produces intermediate or side products that poison the catalyst surface and thereby lead to low reaction rates (current densities) even at fairly high overpotential. With Pt/Sn catalysts it was suggested that the $Sn(OH)_2/Sn(OH)_4$ redox couple (that has a standard potential of +0·075 V referred to hydrogen [5]) acts as a source of oxygen at low potentials. Thus catalysts of the platinum-redox type must be able first

to adsorb methanol and to facilitate electron transfer, and secondly to chemisorb oxygen at a lower potential than on platinum alone and thus minimise poisoning of the surface. The hypothesis of Cathro is that by combining platinum, which has the first property, with tin, which might have the second property, a catalyst is obtained with an enhanced activity over one which has the first property only. Thus Pt/Sn catalysts can be regarded as having dual functions. However, Cathro did not attempt to prove his point by determining the nature of the tin in the electrodeposits. We have, therefore, carried out an investigation of the catalytic, physical and electrochemical properties of Pt/Sn catalysts in an attempt to characterize them further and to understand their function.

2. Experimental

2.1. *Preparation of catalysts*

Pt/Sn electrodeposits were prepared by plating from solutions containing $15 \, g \, l^{-1}$ $SnCl_4 \cdot 5H_2O$ and $21 \, g \, l^{-1}$ $H_2PtCl_6 \cdot 6H_2O$ at a fixed potential of 0·0 V referred to hydrogen. Plating times of 1–10 min were used to give loadings between 0·5 and 5 mg cm^{-2}. The substrate used was in most cases gold foil (adherence to gold is better than to rhodium and rhodium was only used when samples were required for removal and subsequent BET surface area measurement). The pH of the solution was 0·7 and hydrolysis of $SnCl_4$ occurred slowly leading to precipitation of the hydrolysed species after a few hours. Suppression of hydrolysis by addition of HCl, as discussed later, led to less active deposits.

Platinum black electrodeposits were prepared from a solution containing $21 \, g \, l^{-1}$ $H_2PtCl_6 \cdot 6H_2O$ and $0·2 \, g \, l^{-1}$ lead acetate at 0·0 V referred to hydrogen. The small amount of lead was added to improve adherence and to produce a deposit with a high surface area.

2.2. *Physical and chemical characterization of catalysts*

2.2.1. *BET measurements.* Surface areas of deposits vacuum dried at 60° C were measured by the BET method measuring nitrogen adsorption

from a helium carrier using a Shell-Perkin Elmer Sorptometer. Three-point isotherms were measured.

2.2.2. *X-ray powder diffraction* was used to detect any crystalline tin compounds and also to estimate the average size of the platinum crystallites.

2.2.3. *Scanning electron microscopy.* The morphological properties of the deposits were studied using a Cambridge Instruments model S4-10 Scanning Electron Microscope.

2.2.4. *ESCA.* ESCA measurements were performed using an A.E.I. ES 200 spectrometer. The $4f_{7/2}$ spectral line was used for the identification of platinum and the $3d_{5/2}$ line for the identification of tin.

2.2.5. *Neutron activation analysis,* performed at A.E.R.E. Harwell and the University Research Reactor at Risley, was used for the determination of oxygen and chlorine.

2.2.6. *Mössbauer analysis (at A.E.R.E. Harwell)* was used to determine the oxidation state of tin in the bulk of the deposit.

2.2.7. *Wet analyses* of the electrodeposit on rhodium foil were also performed. The deposit was dissolved in hot aqua-regia and tin was determined colorimetrically using salicylidene-amino-2-thiophenol.

2.3. *Electrochemical characterization of catalysts*

2.3.1. *Catalyst activity.* Current-voltage curves were measured in 1 M $CH_3OH/0·25$–6 M H_2SO_4, potentiostatically or galvanostatically using an instrument built in this laboratory. All potentials are referred to a standard hydrogen electrode in the same medium at room temperature. Measurements were made at 25, 60, 80 and 95° C.

2.3.2. *Charging curves and cyclic voltammetry.* Charging curves (chronopotentiometry) were measured by applying a fixed current to an electrode and recording the variation of electrode potential with time. Cyclic voltammograms were measured using a Chemical Electronics
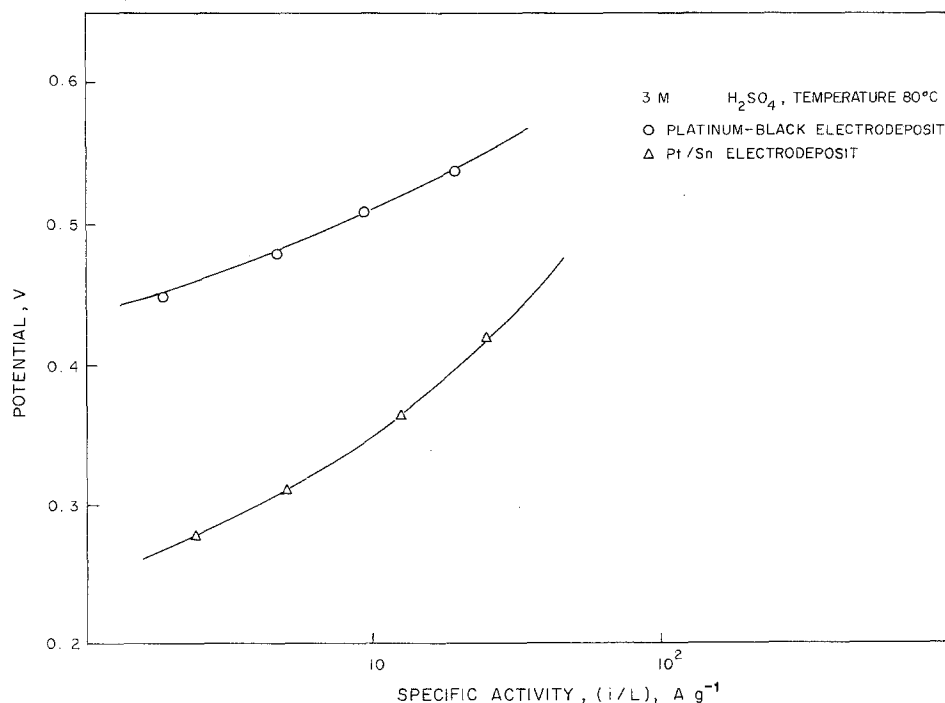
Fig. 1. Comparison of Pt/Sn electrodeposit with platinum-black electrodeposit.

Potentiostat and Waveform Generator in conjunction with a Bryans x—y recorder.

3. Results and discussion

3.1. Activity of Pt/Sn catalysts

The specific activity of Pt/Sn electrodeposits for the oxidation of methanol in 3 M H_2SO_4 is shown in Fig. 1 where it is compared with the performance of platinum black electrodeposit. The specific activity* of Pt/Sn is seen to be some 50 times higher than that of platinum black at 0·4 V.

A more detailed study was made in H_2SO_4 electrolyte where both the temperature-dependence of activity and the effect of electrolyte concentration on activity were studied. From the temperature-dependence the activation energy for Pt/Sn catalysts was found to be 16 ± 1 kcal mol^{-1} compared with 15 ± 1 kcal mol^{-1} for platinum black. The dependence of activity upon H_2SO_4 concentration is shown in Fig. 2. The performance of the catalyst deteriorates considerably

* Specific activity is defined as the current flowing at a particular potential, per unit weight of platinum in the catalyst.

as the electrolyte concentration is increased. Since water is involved in the overall reaction for the oxidation of methanol, this effect is to be expected. However, the decrease in catalyst activity with increasing concentration of acid is greater than the decrease in water activity alone. It seems that poisoning of the active sites on the catalyst occurs (this also occurs for platinum black) by adsorption of bisulphate ion (HSO_4^-) and, at very high acid concentration (>3 M), by undissociated H_2SO_4 molecules. Bisulphate ion is known to adsorb on platinum catalysts and modify the surface [6]. At the same time, Raman spectroscopic studies of H_2SO_4 solutions have shown that the proportion of undissociated H_2SO_4 molecules increases as the total H_2SO_4 concentration is raised [7]. However, from our results it is impossible to differentiate between the possible poisoning effects of these two species.

3.2. Catalyst characterization

The surface area of the Pt/Sn catalysts was dependent on degassing temperature. Degassing temperatures below 80° C produced a BET surface area of 1 m^2 g^{-1}. The highest value found was 4·5 m^2 g^{-1}
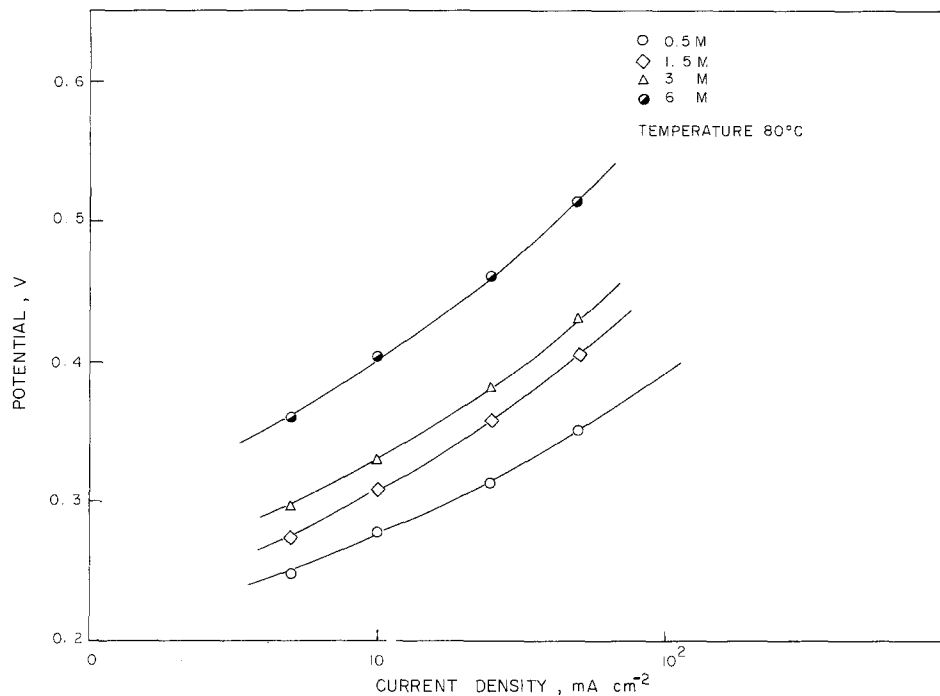
Fig. 2. Influence of H_2SO_4 concentration on the performance of Pt/Sn electrodeposited catalyst.

after degassing at 120° C. The relevance of this higher figure to catalytic activity might be questioned since the catalysts are not degassed at 120° C prior to testing. The BET surface area of our platinum black catalysts was found to be $8 \, m^2 \, g^{-1}$ in reasonable agreement with the electrochemical value of $11 \, m^2 \, g^{-1}$ found by integrating the area under the hydrogen desorption peaks in the cyclic voltammogram of the platinum black electrodeposit and was reasonably independent of degassing temperature above 40° C. Stereoscan pictures of platinum/tin electrodeposits (Figs. 3a–c) in contrast to those of platinum black (Fig. 4) showed a low apparent surface roughness which could perhaps be reconciled with the relatively low BET surface area. It could be argued that the highly porous platinum black is not realizing its true activity because of physical masking of some sites by entrained bubbles of carbon dioxide. If this were so, we would expect some discontinuity in the i–V curves at low currents and none were observed. Moreover preliminary potentiostatic pulse experiments which will form the basis of a later paper are not consistent with such an explanation. On the other hand,

however, X-ray diffraction patterns of Pt/Sn electrodeposits consisted of broad lines corresponding to a mean platinum crystallite diameter of about 10 nm which would be equivalent to a platinum surface area of about $30 \, m^2 \, g^{-1}$. Charging curves also found by Cathro [4], the activity of the than three times the charge required to change the potential of platinum black from 0 to 1·6 V. This would also be consistent with a much higher surface area than found by the BET method and it appears that the BET method does not give reliable results with these Pt/Sn catalysts. As was also found by Cathro [4], the activity of the catalyst is almost linearly dependent upon loading. This would indicate that the deposit is porous. However, the enhancement of activity brought about by the tin over platinum black (50 times) is far greater than any surface area effect as pointed out by Cathro [4]. Our platinum black electrodeposits, as mentioned above, have surface areas of about $10 \, m^2 \, g^{-1}$. and if every platinum atom in a deposit were a surface atom we would have an area of about $300 \, m^2 \, g^{-1}$ which if the available area were directly proportional to activity would give only a factor of 30 improvement. In any case

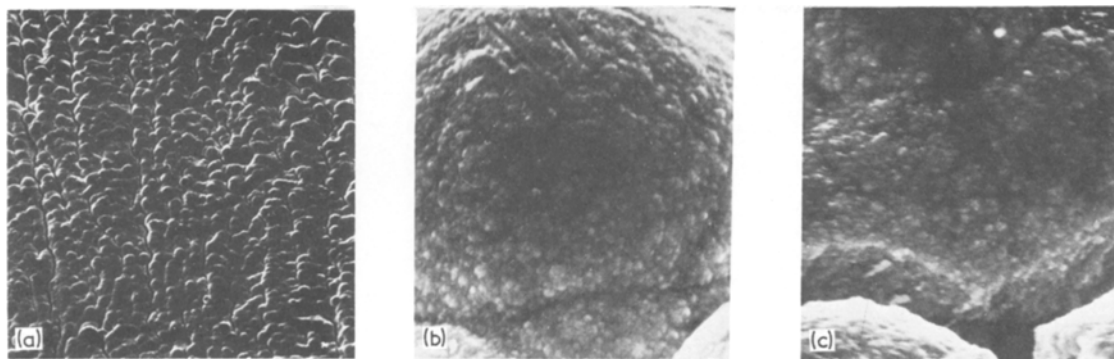Fig. 3. Stereoscan pictures of the surface of platinum/tin electrodeposits. (a) × 1000; (b) and (c) × 10 000.

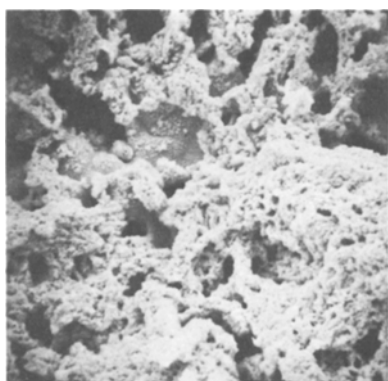

Fig. 4. Stereoscan picture of the surface of platinum black electrodeposit × 1250.

the average crystallite size of 10 nm in the Pt/Sn catalyst is clear evidence that the surface area is much lower than 300 m^2 g^{-1}.

X-ray powder diffraction showed no evidence for alloying between platinum and tin nor were we able to identify any crystalline tin compound. Admittedly, since the deposits contained only up to 6% by weight of tin, it would be difficult to identify any tin compound, especially if it were in a poor crystalline state. Mössbauer spectroscopy showed a main peak of 0.07 ± 0.03 mm s^{-1} accounting for 83% (±8%) of the total absorption with a minor peak at 1.32 ± 0.07 mm s^{-1} accounting for the remainder. The isomer shift of the main peak corresponds to that of tin oxide. The shift of the minor peak corresponds to that of a dilute Pt/Sn alloy. To check the influence of true alloying between Pt and Sn we measured the performance of bulk alloys of composition PtSn and PtSn$_3$ and found high corrosion currents in H$_2$SO$_4$

electrolyte and lower specific activities than those of bright platinum for methanol oxidation. Thus clearly the Pt/Sn electrodeposited catalysts examined were not true alloys though the available data would be consistent with a bulk alloy of composition 99% Pt 1% Sn intimately associated with tin oxide.

The chemical analyses and ESCA results are shown in Tables 1 and 2. Since Mössbauer spectroscopy showed that $83 \pm 8\%$ of the tin in the bulk of the deposit is present as unhydrated tin oxide, the oxygen content is too high to be associated solely with tin. The surface tin oxide is probably present in the hydrated form, and in addition we must presume that part of the platinum in the surface is present as oxidized platinum. This was confirmed by ESCA which showed the presence of Pt(0), Pt(II) and Pt(IV) together with Sn(IV) and indicated the absence of Sn(II) or Sn(0). This is not surprising since at the plating potentials used (0·0 V) we would not expect much Sn(0) to be deposited (Sn(II)→Sn(0) has a standard redox potential of −0·14 V [5]). The standard redox potential for Sn(IV)→Sn(II) is +0·15 V [5] and so Sn(II) might be expected in the deposit; however, this could be oxidized in air to Sn(IV) prior to analysis by ESCA.

The question arises as to how the tin is incorporated in the deposit. Two possibilities are:

(1) Tin forms a chloro-complex with platinum and is co-deposited.
(2) Colloidal tin is incorporated in the platinum matrix in the same way that electrodeposited composite coatings are formed [8].
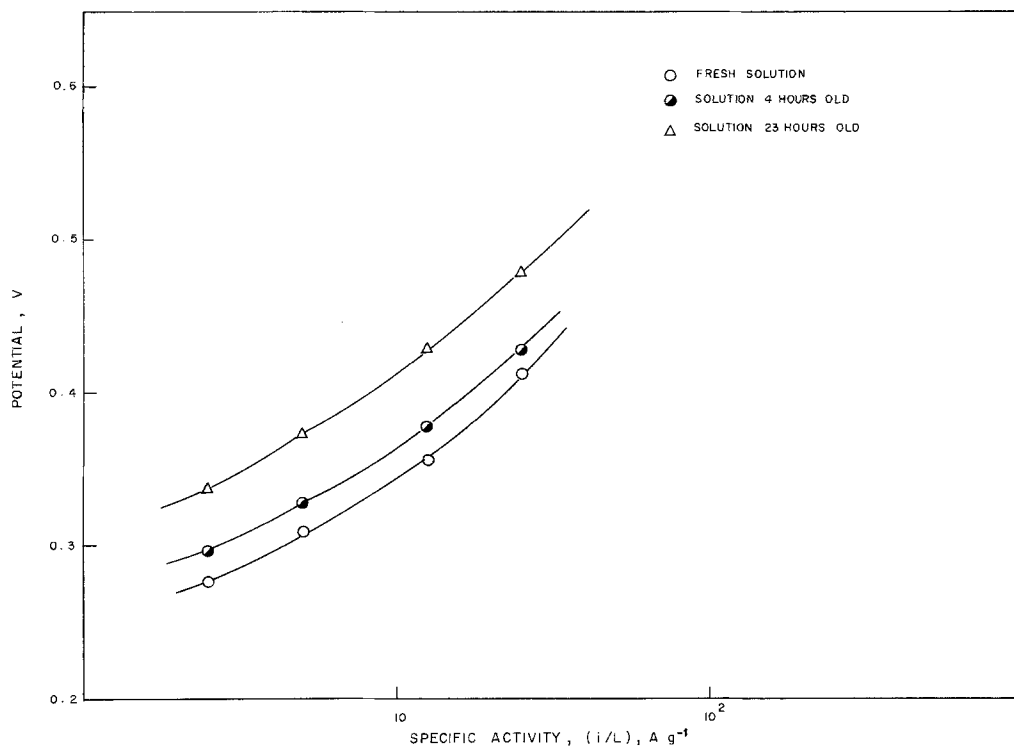
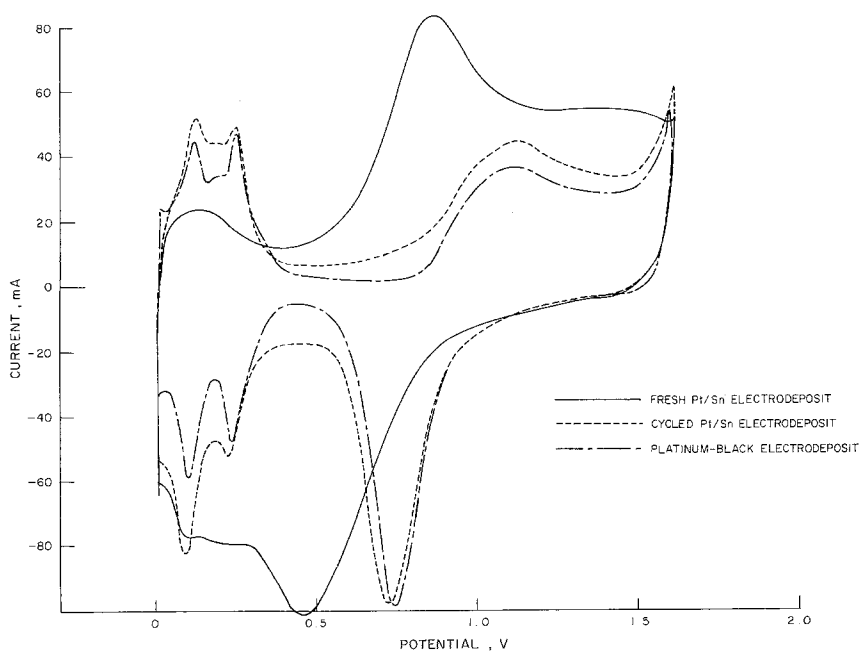Fig. 5. Influence of age of plating solution on Pt/Sn activity.

Fig. 6. Voltammograms for platinum-black and Pt/Sn electrodeposits in 3 M H_2SO_4 at 25° C.

Table 1. Composition of electrodeposits

Sample	Tin content of plating solution (g l^{-1})	Cycled	Tin (wt %)	Oxygen* (wt %)	Chlorine (wt %)	Platinum (wt %)
1	6	No	3·2	3·6	0·9	92·3
5	6	Yes	4·0	2·3	0·11	93·6
7	12	No	4·7	2·5	0·45	92·3
8	12	Yes	4·1	1·3	0·06	94·5

Platinum determined by difference.
* Typical error ±0·3%.

Table 2. Composition of electrodeposits

Sample	Tin content of plating solution (g l^{-1})	Cycled	Tin (at. %)	Oxygen (at. %)	Chlorine (at. %)	Platinum (at. %)
1	6	No	3·6	29	3·3	63
5	6	Yes	4·7	22	0·4	73
7	12	No	5·9	21	1·9	69
8	12	Yes	5·8	13·4	0·3	81
12*	6	No	6	50	—	44†

* Determined by ESCA.
† ~7% as Pt(IV).

Since tin is present in the plating solution exclusively as Sn(IV) the formation of Pt/Sn complexes is unlikely since in these complexes the tin is divalent. The colour of the solution is also different from that of Pt/Sn complex solutions. We further checked this by deliberately making plating solutions containing Pt/Sn complex species; the catalysts obtained from such solutions were very poor. The deposits did in fact contain some chlorine (Tables 1 and 2). However it seems likely that this is present as adsorbed and occluded chloroplatinic or chloroplatinous acid since the chlorine could be removed easily by cyclic voltammetry (Tables 1 and 2).

Light-scattering studies of the mixed electrolyte plating solution showed the presence of colloidal particles even in fresh solutions. The addition of excess HCl which suppresses colloid formation leads to catalysts with activities about one hundredth of those of catalysts prepared from colloidal electrolytes. Thus it seems that colloidal tin is ne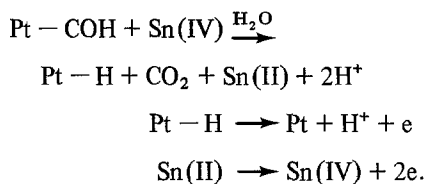cessary to give an active deposit, and tin species are incorporated in the deposit as small particles of oxidized compounds of tin in a platinum matrix. The influence of size of the colloidal species was studied by measuring the activity of catalyst prepared from solutions aged before use for electrodeposition. The results in Fig. 5 show that the size of the colloidal tin species (proportional to the age of the plating solution) determines the catalyst activity. Catalysts containing small tin particles are the most active.

The influence of colloidal materials deliberately or inadvertently added to metal electroplating baths has long been known [9]. These materials can lead to changes in the size of the individual metal crystallites in the deposits. The positively charged colloidal particles themselves may or may not be incorporated in the deposit. Inclusions in the deposit may occur in a number of ways; co-discharge of colloid particles and metal ions; discharge of complex ions containing metal and colloid; adsorption of colloid upon the face of or

within the bulk of the metal deposit. On the basis of our experimental results the latter process would seem to be the most likely.

Thus our results indicate that the major proportion of the tin is not simply modifying the platinum surface by alloying since bulk alloys were inactive and most of the tin is present as oxidized tin. Cyclic voltammetry indicates that the adsorption/desorption of hydrogen, and oxide formation and reduction regions are modified by tin (Fig. 6). These results indicate that the metal surface is to a degree modified. Cycling between 0 and 1·6 V gradually leaches out the tin species until eventually a pure platinum catalyst is obtained. The first few cycles produce an improvement in catalyst performance, probably owing to the removal of some tin species blocking platinum sites, but thereafter the performance deteriorates by leaching of tin from the catalyst.

When methanol is adsorbed on platinum, dehydrogenation takes place leading by stages to Pt–COH residue [10]. It has been suggested by Cathro [4] that the tin in the catalyst could act in a cyclic redox mode enabling the COH residue to be desorbed via a chemical reaction between the adsorbed COH type species and tin according to the following type of scheme:

$$Pt - COH + Sn(IV) \xrightarrow{H_2O}$$

$$Pt - H + CO_2 + Sn(II) + 2H^+$$

$$Pt - H \longrightarrow Pt + H^+ + e$$

$$Sn(II) \longrightarrow Sn(IV) + 2e.$$

If this were the case, then peaks arising from the oxidation and reduction of tin should be observed in the cyclic voltammogram fairly near the redox

potential for the $Sn(OH)_2/Sn(OH)_4$ couple (+0·075 V). However there was no evidence of new peaks at around the theoretical potential of the redox couple though oxygen chemisorption occurs at a lower potential than on platinum alone (Fig. 6). On pure platinum the removal of the residue is effected by interaction with chemisorbed oxygen on the platinum surface, e.g. by a reaction of the type:

$$Pt - OH + Pt - COH \longrightarrow 2Pt - H + CO_2.$$
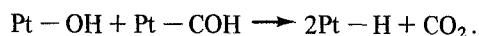
Thus it seems that the earlier onset of oxygen chemisorption on the Pt/Sn catalyst is a possible source of the enhanced activity. Whether the tin is predominately functioning in the redox mode or as a platinum modifier remains at present, however, unresolved.

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