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Pt/Sn bimetallic catalysts for the electro-oxidation of methanol: poisoning by silicate and phosphate anions

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The influence of silicate and phosphate anions on the performance of Pt/Sn electrodeposited catalysts for the electro-oxidation of methanol has been studied. Both anions were found to have serious poisoning effects on the catalyst, whereas platinum catalysts were unaffected. The poisoning mechanism in both cases was thought to be initiated by the formation of either stannosilicates or stannophosphates species followed by the build-up of polymeric silicate or phosphate that ultimately blocks the active sites. The origin of the poisoning mechanism in both cases was found to be chemical rather than electrochemical. In the case of silicate, the poisoning species could be removed and the catalytic activity restored by chemical treatment with sulphuric acid.

1. Introduction

The nature of Pt/Sn-electrodeposited catalysts for the electro-oxidation of methanol in H_2SO_4 electrolyte has been previously studied in some detail [1, 2]. We set out to evaluate the performance of Pt/Sn-electrodeposited catalysts in other electrolytes such as H_3PO_4 and K_2CO_3. In the course of these investigations it was discovered that Pt/Sn catalysts were poisoned by traces of silicate impurity, whilst operating in K_2CO_3 or other alkaline electrolytes. It seemed from these observations that a reaction occurred between the tin species and the silicate ions that resulted in impairment of the tin promoting effects and ultimately in blocking of the platinum sites. In the case of H_3PO_4 electrolyte we have found similar poisoning effects by phosphate ion. This paper presents a more detailed study of the nature of the poisoning mechanism by these anionic species.

2. Experimental

2.1. *Catalyst preparation*

Pt/Sn catalyst was prepared in the manner described previously [2], i.e. plating at an electrode potential of 0·0 V against a bubbling hydrogen electrode from H_2PtCl_6 solution (21 g l^{-1}), containing 15 g l^{-1} $SnCl_4 \cdot 5H_2O$. For comparison platinum-black catalysts were prepared from H_2PtCl_6 solutions by plating at 0·0 V.

2.2. *Catalytic activity*

Current-voltage curves (a direct measure of catalytic activity) were measured potentiostatically or galvanostatically, in 1 M CH_3OH/3 M K_2CO_3 and 1 M CH_3OH/16 M H_3PO_4, using an instrument built in this laboratory. All potentials were measured relative to a bubbling hydrogen electrode at room temperature (25° C). Most catalytic activity measurements were performed at 80° C.

2.3. *Cyclic voltammetry*

Cyclic voltammograms were measured at room temperature, using a Chemical Electronics potentiostat and waveform generator in conjunction with a Bryans x–y recorder.

3. Results and Discussion

Fig. 1 shows the polarization curves for platinum-

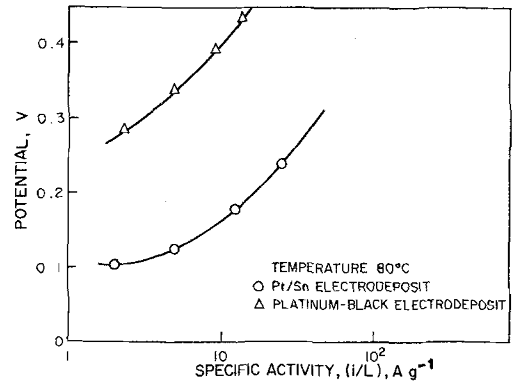

Fig. 1. Performance of platinum-black and Pt/Sn-electrodeposited catalysts for the electro-oxidation of 1 M methanol in 3 M K_2CO_3 electrolyte (glass cell).

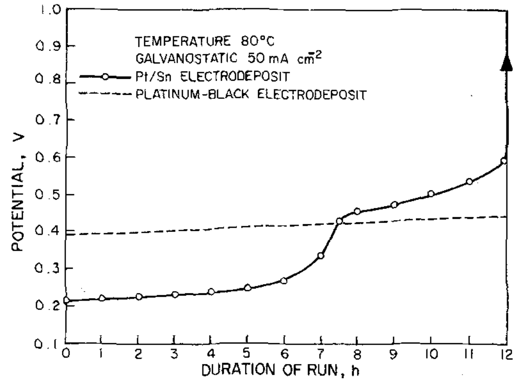

Fig. 2. Stability of Pt/Sn electrodeposit in 3 M K_2CO_3 electrolyte (glass cell).

black and Pt/Sn-electrodeposited catalysts in 3 M K_2CO_3 and 1 M methanol, measured in glass cells at 80° C. As can be seen, the enhancement by tin is similar to that found in H_2SO_4 electrolyte (about 50-fold) described in our previous publication [2]. In addition, the performance of both catalysts in K_2CO_3 electrolyte is considerably better than in 3 M H_2SO_4. The improvement in performance for platinum-black in K_2CO_3, as compared with that for H_2SO_4 for methanol electro-oxidation, has been described in detail by Beltzer [3]. In view of the attractive activity of the Pt/Sn catalyst, it was decided to measure the stability of the catalyst over longer periods of time in 3 M K_2CO_3. This experiment was conducted in a glass cell. The dependence of activity on test duration is shown in Fig. 2[*]. The activity shows a gradual decrease over the first six hours, probably because of the build-up of bicarbonate ions in the electrolyte layer adjacent to the catalyst [3]. After 6 h, a more dramatic decrease in activity occurs that lowers the activity in a very short space of time to that of pure platinum black. Thereafter a further gradual decrease in activity occurs until eventually after twelve hours there is a complete loss of activity. The loss in activity (after 6 and 12 h respectively) seems to be associated with the tin function in the catalyst since platinum-black did not show this effect (Fig. 2). This suggests that something in the electrolyte was poisoning the tin (stability tests in H_2SO_4 electrolyte did not show this effect).

Chemical analysis of the K_2CO_3 electrolyte revealed the presence of about 0·1 wt % Si, that would appear to originate from the glass cell. A possible source of poisoning might therefore be the silicate ion, i.e. $(HO)_2SiO_2^{2-}$, or polymeric silicates. Consequently, the life test was repeated with a fresh sample of catalyst in a Teflon vessel in which all ancillary parts, i.e. Luggin capillary, counter electrode and in-situ Giner-type reference electrode [4], were constructed from Teflon. The results of this test are shown in Fig. 3. As can be seen, only the gradual decrease in activity owing to build-up of bicarbonate ions is found. In a second life test, 1·5 ml of K_2SiO_3 solution was added (1·33 g K_2SiO_3 ml^{-1}) after 4 h. The effect on the activity was quite dramatic (Fig. 3); within a short time activity was completely lost, thus confirming that the poisoning agent was indeed the silicate anion.

The polarization curve for Pt/Sn catalyst in

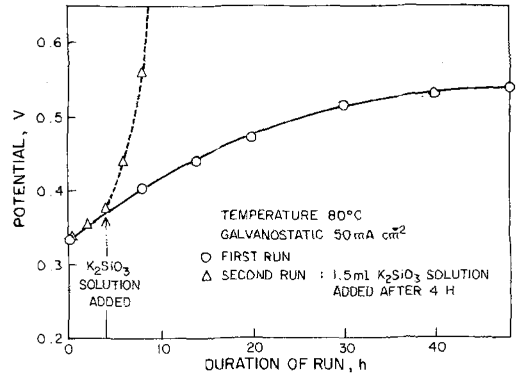

Fig. 3. Stability of Pt/Sn electrodeposit in 3 M K_2CO_3 electrolyte (Teflon cell).

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[*] Increase in potential at a constant current density indicates a decrease in catalytic activity.

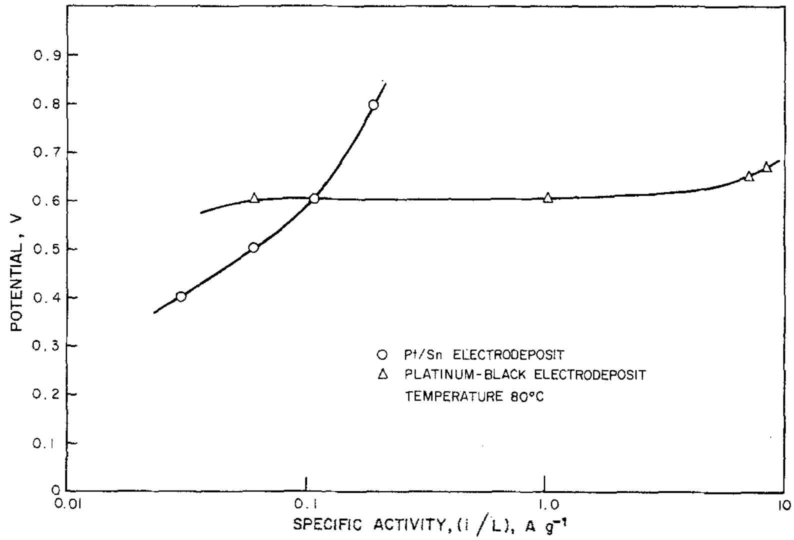


Fig. 4. Performance of Pt/Sn electrodeposit for methanol electro-oxidation in 16 M H_3PO_4.

16 M H_3PO_4 at 80° C is shown in Fig. 4. The performance was considerably poorer than the performance of platinum black in the same electrolyte. We have shown previously that the enhancement brought about by tin is similar in both acid and basic electrolytes; thus the fact that Pt/Sn catalyst was found to be poorer than platinum black in H_3PO_4 electrolyte would indicate that something in the electrolyte, possibly one or other of the phosphate anions, selectively poisons the tin species in an analogous way, perhaps, to the poisoning effect already discussed for silicates. The structures of $(HO)_2SiO_2^{2-}$ and $(HO)_2PO_2^{1-}$ are similar, and phosphate is known to substitute for silicate in a number of silicate and aluminosilicate lattices [5]. Thus reactions between tin and silicates or phosphates might be expected to be similar. In a previous publication [2] we have shown that the majority of the tin is present on the catalyst surface as a hydroxylated compound of tin oxide – thus possibilities exist for reaction of the tin oxide with the two poisons mentioned by condensation between hydroxyl groups.

Fig. 5 shows cyclic voltammograms of a typical

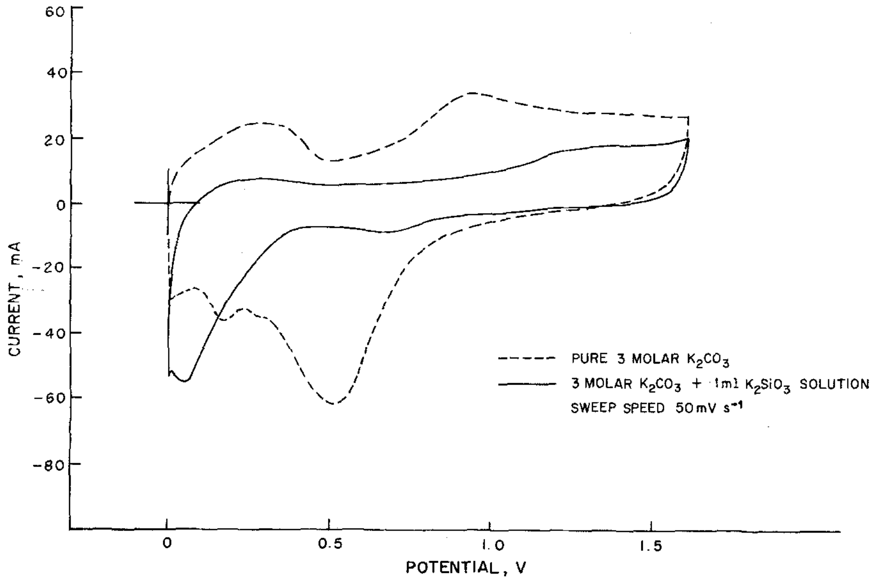


Fig. 5. Cyclic voltammograms of Pt/Sn electrodeposit in 3 M K_2CO_3 and 3 M K_2CO_3 + 1 ml K_2SiO_3 solution.

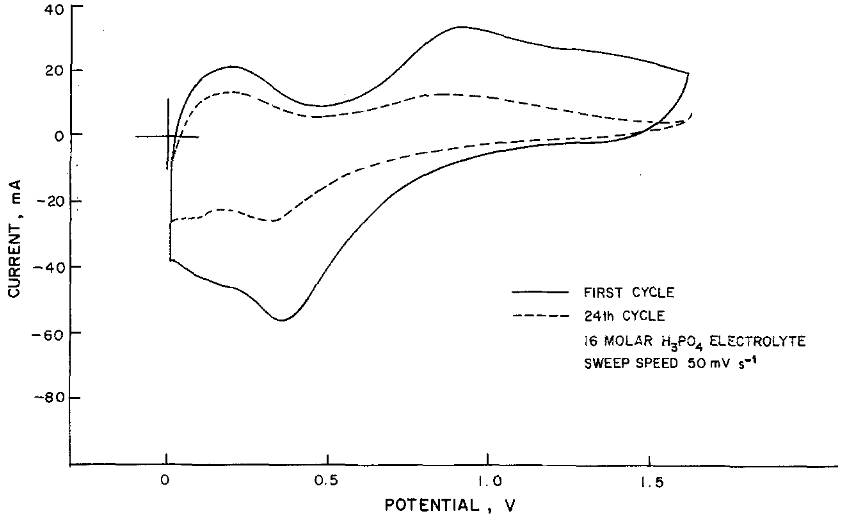


Fig. 6. Cyclic voltammograms of Pt/Sn electrodeposit in 16 M H_3PO_4.

Pt/Sn electrodeposit in 3 M K_2CO_3 in the absence and in the presence of added K_2SiO_3 solution. The profile of the voltammogram in the presence of added silicate (0·1 wt%) is considerably changed from that found for pure 3 M K_2CO_3. First, whereas contained cycling of the Pt/Sn catalyst between 0 and 1·6 V in K_2CO_3 electrolyte leads to the gradual stripping of tin from the deposit, the addition of silicate ions stabilizes the profile and no change occurs with repeated cycling. Secondly, the hydrogen desorption, oxygen chemisorption and platinum oxide reduction regions are considerably reduced in intensity in the presence of silicate ions, indicating that the active area for chemisorption is smaller. Finally, a new peak appears on the cathodic sweep in the hydrogen adsorption region that is too intense to be accounted for by hydrogen adsorption and probably arises from reduction of some unidentified oxide species formed on the anodic cycle above about 1·2 V.

The results in H_3PO_4 electrolyte (Fig. 6) are quite similar. On the first cycle the profile of the voltammogram is comparable with that of Pt/Sn catalyst in 3 M H_2SO_4 (Fig. 7), but on subsequent cycling the area under the profile is considerably reduced although there are no major changes in the features of the profile. Eventually, after about 30 cycles in H_3PO_4, the voltammogram becomes almost completely featureless and the peaks at 0·9 V on the anodic cycle and at 0·35 V on the cathodic cycle have largely disappeared (Fig. 6). This behaviour is in complete contrast to that of the same type of catalyst in H_2SO_4 where, on prolonged cycling, tin is lost and the voltammogram becomes similar to that of pure platinum (Fig. 7). Thus, it seems that in H_3PO_4 electrolyte both the tin and platinum on the catalyst surface are becoming buried in some way by a poisoning agent. Qualitatively, there are strong similarities between the effects of silicate and phosphate and the poisoning mechanisms involved may be related.

The question arises as to whether the effect is brought about electrochemically or simply by a chemical interaction with the catalyst surface. Thus, we immersed a Pt/Sn catalyst in 3 M K_2CO_3 electrolyte containing the same concentration of K_2SiO_3 as was added during the cyclic voltammetric studies. The duration of this treatment was ten days at 25° C. The catalyst was removed from the electrolyte, washed with distilled water and cycled in pure 3 M K_2CO_3. The voltammogram is shown in Fig. 8, curve a, and is seen to be similar to that obtained when K_2SiO_3 was added previously. Thus, the poisoning effect of silicate ion is chemical in nature. To check whether the effect was reversible, we immersed the poisoned catalyst in 3 M H_2SO_4 at 80° C for a few minutes and then measured a polarization curve. The catalyst performance was only slightly poorer than that of a fresh unpoisoned Pt/Sn catalyst. On subsequent cycling in 3 M K_2CO_3 (Fig. 8, curve b), an identical profile to that of pure unpoisoned Pt/Sn

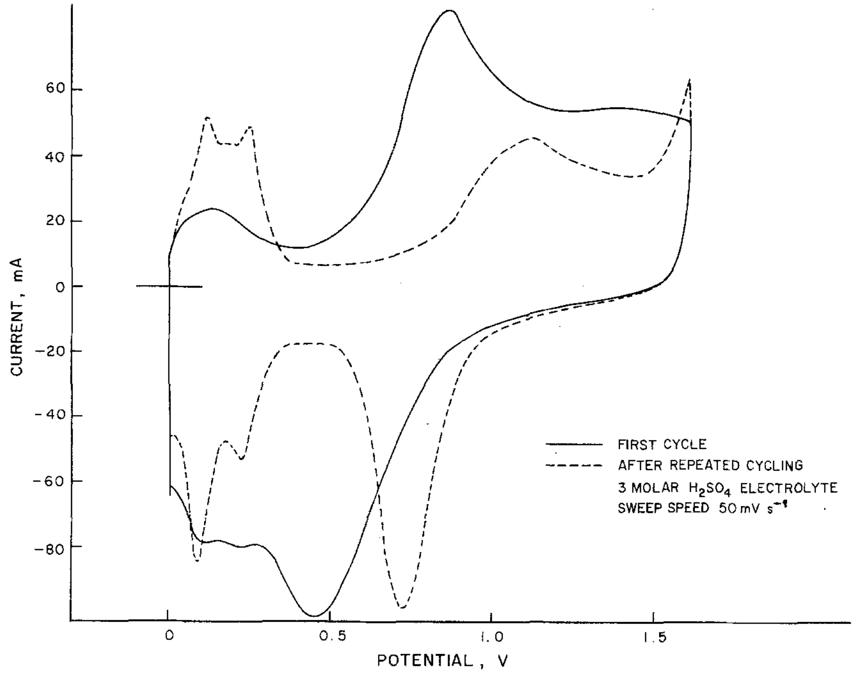


Fig. 7. Cyclic voltammograms of Pt/Sn electrodeposit in 3 M H_2SO_4.

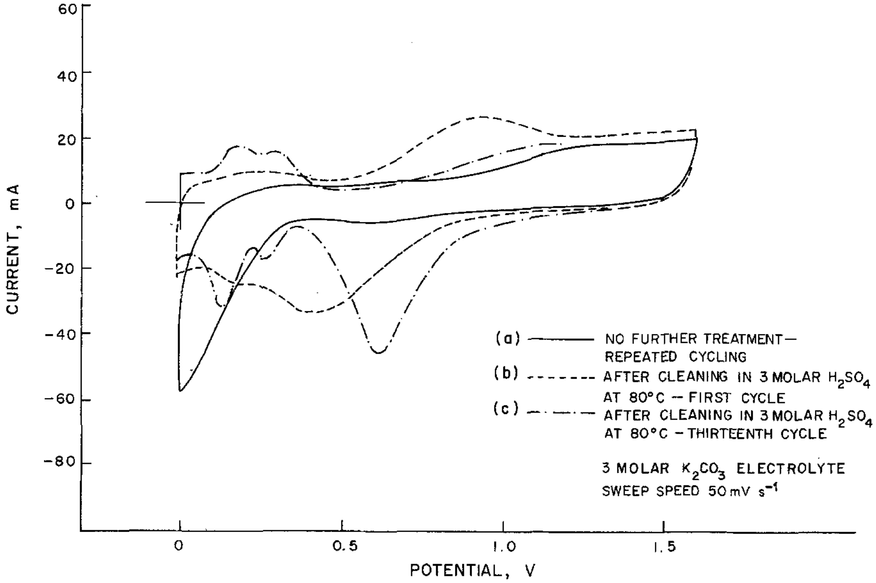


Fig. 8. Cyclic voltammograms of Pt/Sn electrodeposit after immersion in 3 M K_2CO_3 containing K_2SiO_3 for 10 days at 25° C.

catalyst was found, indicating thus that the silicate could be removed chemically. Subsequent behaviour on cycling was also characteristic of unpoisoned Pt/Sn electrodeposit (Fig. 8, curve c).

A fresh Pt/Sn catalyst was immersed in H_3PO_4 electrolyte at 25° C for 10 days and then washed with distilled water and cycled in 3 M H_2SO_4. Voltammetry profiles were similar to those found

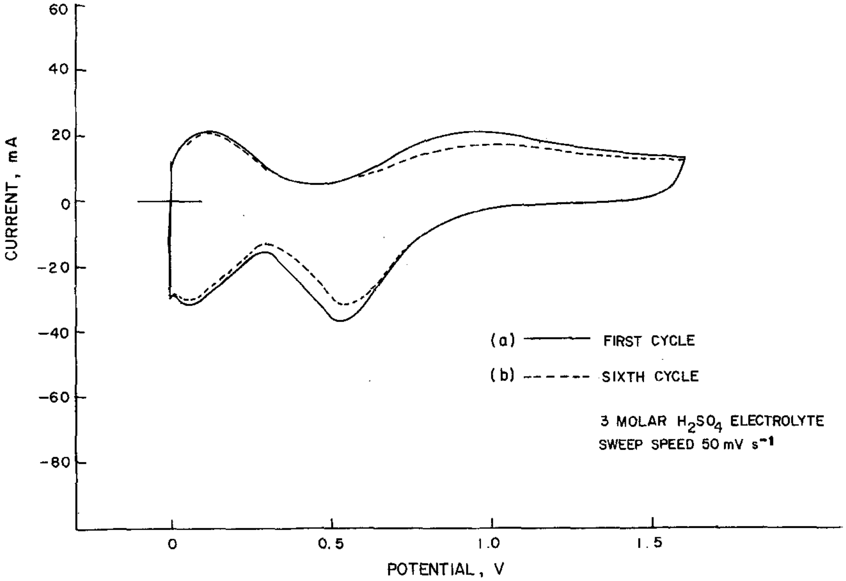
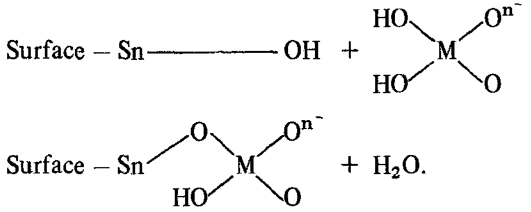


Fig. 9. Cyclic voltammograms of Pt/Sn electrodeposit after immersion in 16 M H_3PO_4 for 10 days at 25° C.

previously with H_3PO_4 electrolyte (Fig. 9, curves a and b), i.e. no leaching of tin occurred on cycling, but reductions in intensity of the oxide formation and reduction regions were found without any compensating appearance of peaks due to oxide formation on free platinum. Treatment with 3 M H_2SO_4 at 80° C did not reverse the poisoning effect of the phosphate ion.

Since platinum-black electrodeposits are comparatively unaffected by silicate or phosphate ions, the question arises as to the nature of the poisoning mechanism since in both cases the platinum in Pt/Sn catalysts is also affected. From our cyclic voltammetry studies, it is clear that in both cases the poisoning effect is, in essence, blocking of the catalyst sites. This blocking effect is initiated (or catalysed) by the tin centres and subsequently covers the platinum sites also. In a typical Pt/Sn deposit the atomic ratio of Sn/Pt is about 0·15 and, from previous work, the surface tin oxide appears to be hydrated [2]. The surface of the catalyst could be envisaged as an array of platinum-metal crystallites in which particles of hydroxylated tin are embedded. Now silicates and phosphates, whether monomeric or polymeric, will also be hydroxylated and we envisage the poisoning reaction as being as follows (where we have chosen, for simplicity, monomeric poisoning species)



If this reaction occurs at the various tin oxide sites on the catalyst surface, then further intermolecular condensation reactions might occur until not only the tin oxide sites but also the platinum sites between the respective surface tin sites are blocked. The whole process can be regarded as a build-up of a silicate or phosphate framework initiated by preliminary stannosilicate or stannophosphate formation. Any charge balance required for such a framework structure would come from hydrogen ions in the case of phosphate poisoning, and from potassium ions in the case of silicate poisoning. The initial effect catalytically would be the destruction of the function of the co-catalyst and ultimately complete loss of activity upon poisoning of the platinum catalyst. This is clearly what is occurring during the stability test conducted in the glass vessel (Fig. 2). The first loss of activity after 6 h results from poisoning of the tin species by the condensation reaction already described. During the second gradual decrease in activity between

6 and 12 h the silicate framework grows between tin centres on the catalyst until eventually the platinum sites are made inaccessible to methanol and activity is completely lost. In the case of phosphate poisoning the concentration of phosphate is so high that poisoning of some platinum sites occurs almost immediately, leading to activities much lower than that of platinum black.

This investigation indicates that where a bimetallic electrocatalyst consists of platinum associated with an oxide or hydroxide of a second metal then possible poisoning effects by hydrated monomeric or polymeric anions might be severe owing to reaction with the hydroxylated surface of the co-catalyst.

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