

Electrolytes for methanol–air fuel cells.

I. The performance of methanol electro-oxidation catalysts in sulphuric acid and phosphoric acid electrolytes

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Phosphoric acid and sulphuric acid have been compared as potential electrolytes for methanol–air fuel cells. The performances of typical electro-oxidation catalysts were measured in both electrolytes over a range of concentrations. With all catalysts the activity falls with increasing acid concentration. While this is to some extent due to the decrease in water activity at higher concentrations it seems that with both acids there is significant poisoning of the catalyst. The results can be explained for both electrolytes by assuming that adsorption of undissociated acid poisons the catalyst surfaces and that the reaction rate on the poisoned surfaces is proportional to the water activity.

1. Introduction

In the search for the commercial methanol–air fuel cell, a possible alternative or complement to the discovery of highly active catalysts is the use of acid electrolytes other than sulphuric acid. The reason that catalysts have differing performances in different electrolytes depends on several factors, one of which is the poisoning effect caused by adsorption of electrolyte on the catalyst surface.

Ideally we would prefer to use acids such as perchloric acid, which has only a minimal poisoning effect, but, for safety reasons, this acid could probably not be used in a commercial system. Of the common acids we have to rule out hydrochloric acid, since Cl is a well-established poison for platinum, and also nitric acid, because of its oxidizing nature. The only common acid other than sulphuric acid for this application is phosphoric acid.

Phosphoric acid has a much poorer conductivity than sulphuric acid, but has the advantage of being usable at higher temperatures. Sulphuric acid above about 100°C is reduced and this leads to poisoning of platinum activity by sulphide species. Phosphoric acid is stable to at least 180°C and

considerable work is reported in the literature on the use of phosphoric acid as electrolyte for hydrocarbon–air [1] and hydrogen–air [2] fuel cells. Relatively little work has been done on the use of phosphoric acid as an electrolyte in methanol–air fuel cells, most studies being confined to low-temperature work using sulphuric acid. Therefore, we have undertaken a comparison of the performances of conventional methanol electro-oxidation catalysts such as platinum-grey, platinum-black, Adams platinum/ruthenium and platinum/tin electrodeposits in phosphoric acid and sulphuric acid. In this paper the influence of electrolyte concentration and temperature on the performance of the above catalysts is discussed and an evaluation is given of the potential application of phosphoric acid in methanol–air fuel cells.

2. Experimental

Electrolytes. Analar H₂SO₄ and Analar H₃PO₄ (88% wt.) were used without purification as starting materials. Dilute solutions were made up with distilled water.

Catalysts. Adams Pt/Ru (70% wt. Pt 30% wt. Ru), was made into electrodes by spraying from a

solution of CCl_4 containing 1% wt. low-density polyethylene binder onto pre-etched gold foil. For gas-diffusion electrodes the substrates were sintered PVC, microporous polypropylene and filled carbon fibre paper. Pt/Sn electrodeposits were prepared on pre-etched gold foil by plating at a potential of +0.050 V relative to the bubbling H_2 reference electrode from a solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (21 g l^{-1}) and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (15 g l^{-1}). Pt-grey electrodeposit was made by plating from a solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ at +0.050 V. Pt-black was made by plating from a solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (21 g l^{-1}) to which 0.2 g l^{-1} Pb acetate was added.

2.1. Catalytic activity measurements

Polarization curves (a measure of catalytic activity) were measured galvanostatically in a conventional three-armed glass cell at temperatures between 25 and 95°C , using a galvanostat built in this laboratory. The concentration of methanol in the electrolytes was constant at 1 M.

2.2. Cyclic voltammetry

Cyclic voltammograms were measured using a potentiostat and waveform generator built in this laboratory in conjunction with a Bryans X-Y recorder.

3. Results and discussion

The performances of Adams Pt/Ru and Pt/Sn electrodeposits in different concentrations of H_2SO_4 are shown in Fig. 1 which shows that the activity is reduced by a factor of 4 in changing from 0.5 M to 3 M H_2SO_4 .

As the H_2SO_4 concentration is increased the following changes take place in the solution:

- (1) The water activity drops.
 - (2) The concentrations of HSO_4^- and of undissociated H_2SO_4 molecules increases.
 - (3) The hydrogen ion concentration increases.
- The possible effects of these variables have been considered as follows.

Firstly, the drop in performance with increasing acid concentration seems too great to be explained by a decrease in water activity alone (the activities of water in 3.0 M and 0.5 M H_2SO_4 are about 0.8 and 0.98, respectively). Secondly, a measurement of catalytic activity in a mixed electrolyte of 0.5 M H_2SO_4 /1 M KHSO_4 has been made and the activity of Pt/Sn in this mixed electrolyte was found to be only one-half of that in pure 0.5 M H_2SO_4 . This is the same reduction in activity found on changing from 0.5 to 1.5 M H_2SO_4 and this suggests that HSO_4^- has a poisoning effect. In addition, of course, the role of undissociated H_2SO_4 molecules must be considered, but published concentrations of HSO_4^-

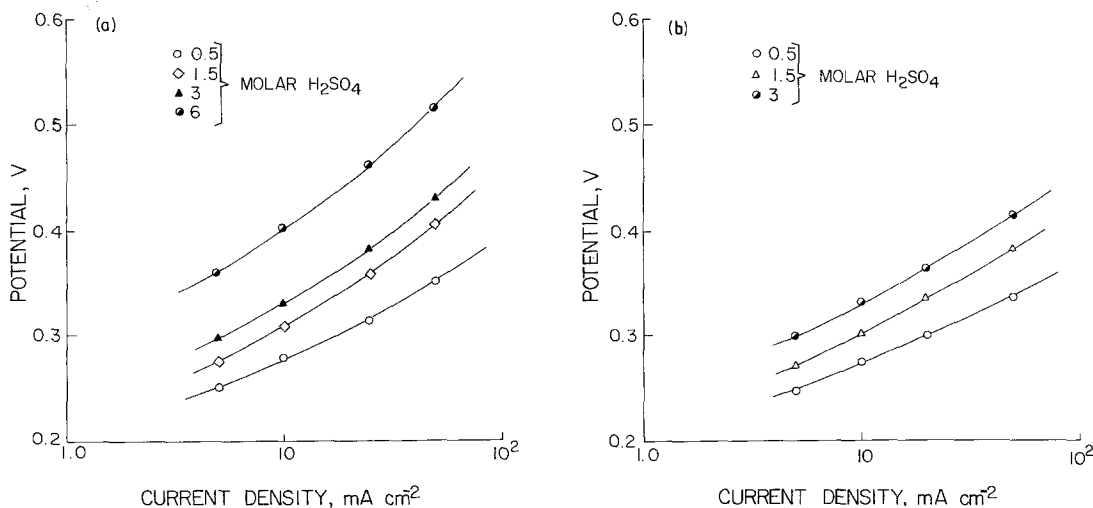


Fig. 1. Influence of H_2SO_4 concentration on the performance of (a) Pt/Sn electrodeposited catalyst; (b) Pt (70% wt.)/Ru (30% wt.) Adams catalyst. Temperature = 80°C .

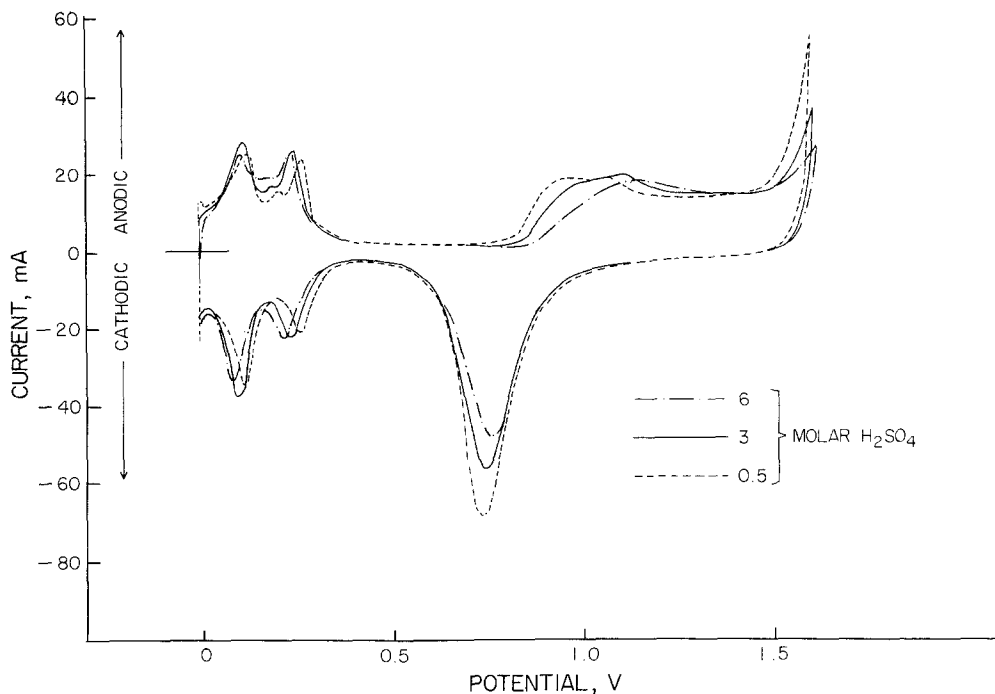


Fig. 2. Cyclic voltammograms of platinum-black in various concentrations of H_2SO_4 : temperature = 25°C ; sweep speed 50 mV s^{-1} .

and undissociated H_2SO_4 as determined by Raman spectroscopy [3] indicate that up to at least 3 M, the predominant species is HSO_4^- . However, it may be that the small amount of undissociated H_2SO_4 present at these concentrations is more strongly adsorbed on Pt than is HSO_4^- and, as a result, is the main source of the poisoning effect.

We have also examined the state of the platinum catalyst surface in different concentrations of H_2SO_4 using cyclic voltammetry. This study was confined to platinum-black since both Pt/Sn and Pt/Ru are subject to either tin or ruthenium stripping using this technique. The results are shown in Fig. 2. While there are qualitative changes in the profile in the H_2 adsorption and desorption regions with increasing acid concentration, there is little change in overall intensity. As the acid concentration is increased the potential at which oxidized platinum species start to form also increases. It seems that the chemisorption of oxygen on Pt is retarded by some entity or entities in the electrolyte whose concentration increases with increasing electrolyte concentration. This can only be HSO_4^- ions and/or undissociated H_2SO_4 molecules. Since HSO_4^- ion is known to modify the O_2 chemisorption region on platinum [4] and since

additions of KHSO_4 to dilute H_2SO_4 solutions produced similar changes in the cyclic voltammetry profile it seems certain that HSO_4^- ion is at least partly the origin of this blocking effect. Moreover Fig. 1 suggests that this effect has become serious when the concentration of H_2SO_4 is about 3 M.

Similar results, i.e. performance decreasing with acid concentration, are also found with phosphoric acid electrolyte. Figs. 3(a) and (b) compare typical results in H_3PO_4 with the performance in 3 M H_2SO_4 at 80°C and it is clear that under all the conditions studied the results are inferior in H_3PO_4 and that the more dilute the H_3PO_4 electrolyte, the better the catalyst performance.

In order to investigate the influence of acid concentration more comprehensively, a more detailed comparison of the two acids was made. It was considered that the problem might be tackled by making comparative measurements in the two acids using concentrations chosen to give constant water activity (a_w). Since the activity of water in sulphuric acid is known [5], it was only necessary to estimate the activity of water in phosphoric acid. This was done as follows.

At equilibrium the chemical potential of a

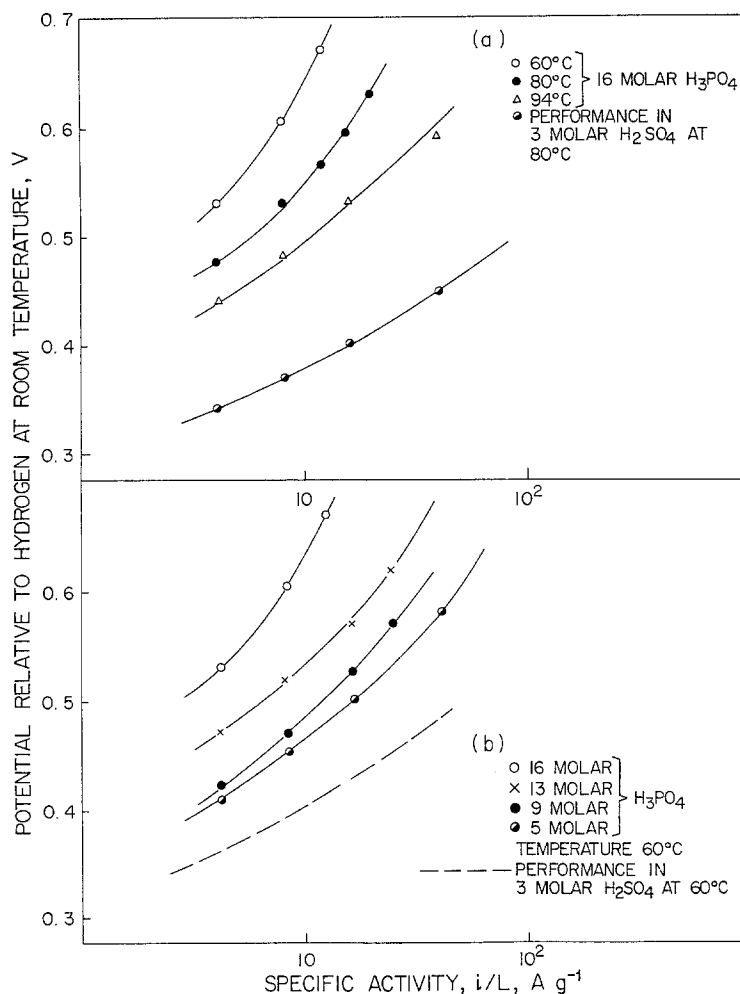


Fig. 3. 70% wt. Pt 30% wt. Ru Adams catalyst in phosphoric acid: (a) effect of temperature; (b) effect of electrolyte concentration.

species must be the same in both the condensed and vapour phases. If gas imperfections are ignored, it follows that $a_w = P_w/P_w^0$, where P_w is the vapour pressure of water above the acid solution and P_w^0 the vapour pressure of water above pure water. Fig. 4 gives values of a_w and P_w/P_w^0 for sulphuric acid solutions (showing good agreement) and values of P_w/P_w^0 for solutions of phosphoric acid. Fig. 4 was used to select appropriate acid concentrations. Chosen conditions were 1 M H_2SO_4 and 3.2 M H_3PO_4 ($a_w = 0.96$), 3.4 M H_2SO_4 and 5.9 M H_3PO_4 ($a_w = 0.8$), 6.1 M H_2SO_4 and 9.7 M H_3PO_4 ($a_w = 0.5$), and 8 M H_2SO_4 and 12.4 M H_3PO_4 ($a_w = 0.26-0.3$). The activities of platinum-grey electrodeposit, platinum-black electrodeposit and Pt/Ru (70% wt. Pt, 30% wt. Ru) Adams catalyst were

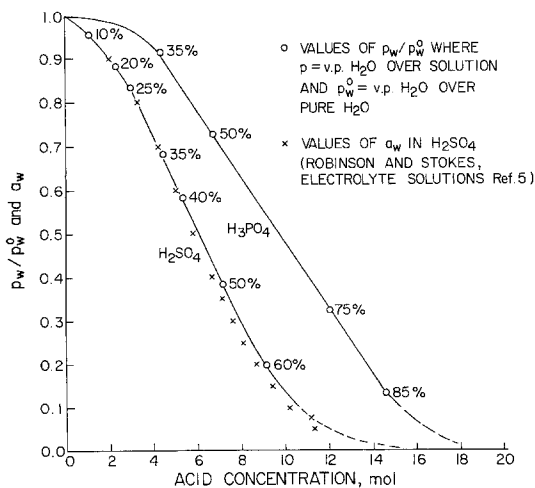


Fig. 4. Calculation of water activity in phosphoric acid from vapour pressure data (data for sulphuric acid shown for comparison).

measured in these electrolytes. The specific activities of the three catalysts as a function of acid concentration are shown in Figs. 5-7. The results for all three catalysts are similar. The general conclusions are that in phosphoric acid the activities of the catalysts fall off linearly with increasing acid concentration (the relationship for platinum-grey is slightly non-linear), whereas with sulphuric acid the specific activities of all three catalysts fall off more dramatically at acid concentrations above 3 M. The effect in both acids, as implied earlier, is greater than expected from the drop of water activity with increasing acid concentration and a possible explanation is that poisoning by sulphuric acid species is more drastic than that by phosphoric acid species.

We have suggested earlier that HSO_4^- adsorption on platinum inhibits the oxidation of methanol in the range 0.5-3 M H_2SO_4 . However, the results presented here suggest that adsorption of undissociated acid might lead to poisoning of methanol oxidation catalysts above 3 M. This seems particularly likely for phosphoric acid where dissociation is small ($K_1 = 7.5 \times 10^{-3}$) and the concentration of H_2PO_4^- will remain small over the whole range

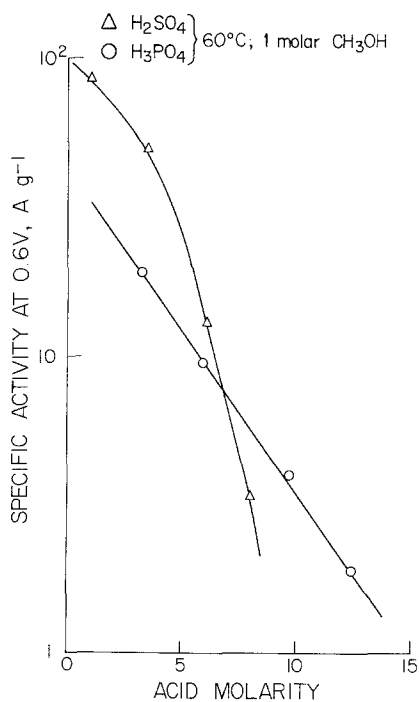


Fig. 6. Dependence of platinum-black activity on electrolyte concentration.

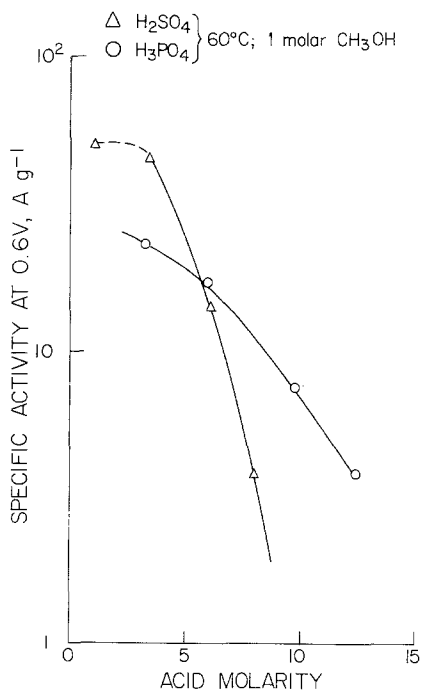


Fig. 5. Dependence of platinum-grey activity on electrolyte concentration.

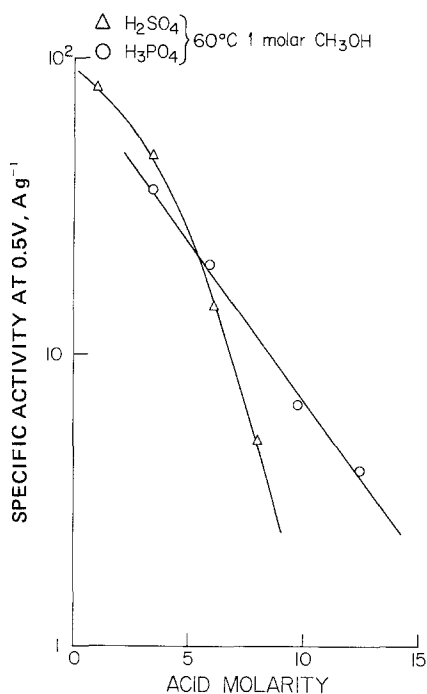


Fig. 7. Dependence of 70% wt. Pt/30% wt. Ru Adams catalyst activity on electrolyte concentration.

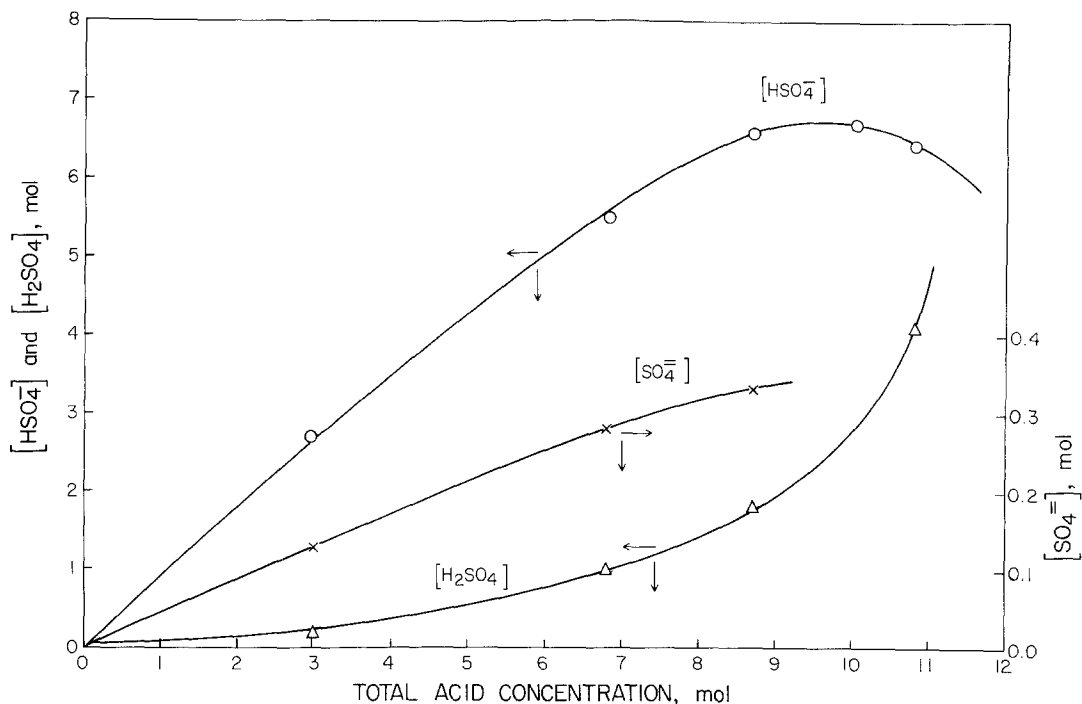


Fig. 8. Relationship between species present in H_2SO_4 and total acid concentration.

of acid concentration used in this work. We have therefore tried to quantify our results on the basis of a simple model.

It is known that over a wide range of conditions most of the surface of a platinum electrode is covered by organic residues and that at low currents the steady-state fractional surface coverage is about 0.7–0.8. The rate-determining step involves the oxidation of these residues by an oxygen-containing species such as OH_{ad} , $\text{H}_2\text{O}_{\text{ad}}$ or water in the vicinity of the electrode. We consider the case where adsorbed water (or OH_{ad}) is the participating species and assume that this species can only occupy sites free from strongly adsorbed, undissociated acid. Then if the adsorption of acid is Langmuirian

$$k_1 C_a (1 - \theta_{\text{org}} - \theta_a) = k_1^1 \theta_a \quad (1)$$

where C_a is the concentration of acid and θ_{org} and θ_a are the fractional coverages by organic residues and acid respectively. Then the fraction of the surface available for water adsorption equals

$$(1 - \theta_{\text{org}} - \theta_a) = \frac{k_1^1 (1 - \theta_{\text{org}})}{k_1 C_a + k_1^1} \quad (2)$$

Using this simple model the concentration of adsorbed water was taken as proportional to

$$\frac{k_1^1 (1 - \theta_{\text{org}}) a_w}{k_1 C_a + k_1^1} \quad (3)$$

where a_w is the activity of water in solution. Then the current (i) can be expressed as

$$i = \frac{k \theta_{\text{org}} k_1^1 (1 - \theta_{\text{org}}) a_w}{k_1 C_a + k_1^1} \quad (4)$$

or

$$\frac{a_w}{i} = \frac{k_1 C_a + k_1^1}{k \theta_{\text{org}} k_1^1 (1 - \theta_{\text{org}})} \quad (5)$$

and, if θ_{org} is invariant with C_a , as seems to be the case, plots of a_w/i against C_a should be linear.

Moreover the ratio of slope/intercept has the value of k_1/k_1^1 and gives an indication of the strength of adsorption of the acid. For phosphoric acid the concentration of undissociated acid will be almost equal to the total acid concentration. For sulphuric acid the concentrations of SO_4^{2-} , HSO_4^- and undissociated acid, as determined by Raman spectroscopy, are available in the literature [3]; this information is given in Fig. 8 and has been used to interpret our results.

Plots of the relationship a_w/i against the concentration of undissociated acid are shown in Figs. 9 and 10 for phosphoric and sulphuric acid, respectively, and reasonably good straight lines

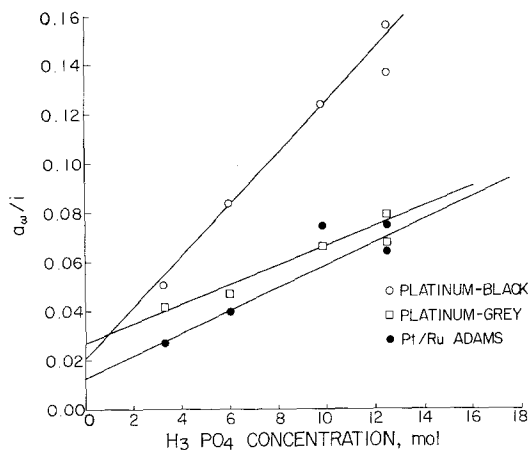


Fig. 9. Dependence of a_w/i on H_3PO_4 concentration.

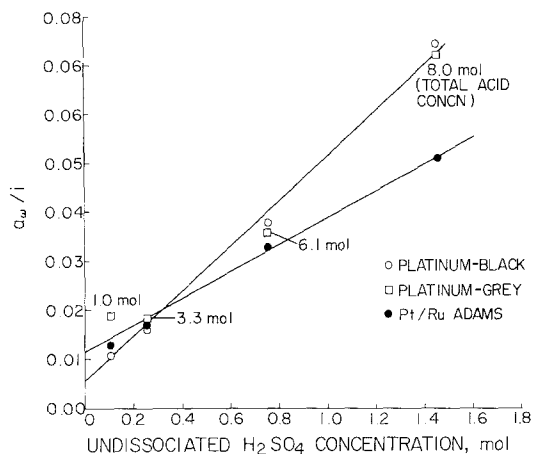


Fig. 10. Dependence of a_w/i on the concentration of undissociated H_2SO_4 .

result. (Plots of a_w/i against HSO_4^- and SO_4^{2-} did not give straight lines.) From Figs. 9 and 10 the ratios of k_1/k_1^I have been determined for the various catalysts studied. The results are shown in Table 1. These results indicate that our qualitative conclusion may be correct, i.e. that sulphuric acid, in its undissociated form, is much more strongly adsorbed than is phosphoric acid. This accounts for the more rapid fall-off of catalytic activity in sulphuric acid at concentrations above about 3 M (where the concentration of the undissociated acid is becoming high). It also appears that undissociated sulphuric acid may be much more strongly adsorbed than HSO_4^- .

On the basis of the work described so far it is

Table 1. Values of k_1/k_1^I for catalysts studied (determined from Figs. 9 and 10)

Catalyst	k_1/k_1^I	
	H_2SO_4	H_3PO_4
Platinum-black	8.36	0.53
Platinum-grey	8.36	0.16
Pt/Ru Adams	2.39	0.39

clear that catalyst performance is superior in sulphuric acid in spite of the poisoning effect of solution species. However, sulphuric acid cannot be used at temperatures above about $100^\circ C$ and the use of phosphoric acid may offer some advantage at sufficiently high temperatures. At such temperatures it will not be possible to use dissolved methanol in a complete fuel cell and a limited study of the use of methanol vapour was undertaken. Pt/Ru catalysts mounted on sintered PVC substrate, microporous polypropylene and filled carbon paper, were tested at $95^\circ C$ in 16 M H_3PO_4 using methanol vapour and their performances were compared with that of a Pt/Ru Adams electrode using dissolved methanol fuel at the same temperature. The results are shown in Fig. 11. The vapour diffusion electrode gives an activity that is significantly higher than that of the dissolved fuel electrode but shows limiting current behaviour above about 0.42 V.

4. Conclusions

From the results reported here it is apparent that in low temperature methanol-air fuel cells ($< 60^\circ C$), where with 3 M H_2SO_4 the water-balance problem would be minor, this electrolyte would be superior to H_3PO_4 at any concentration. At higher temperatures, however, where to maintain water-balance higher concentrations of H_2SO_4 would be essential, the difference in activity between catalysts in H_2SO_4 and H_3PO_4 of comparable water activity is much lower. At temperatures above $90^\circ C$ the performances of some methanol electro-oxidation catalysts, when used with gaseous fuel, are quite reasonable in 16 M H_3PO_4 , and at even higher temperatures the use of this electrolyte could be attractive. However, the performance in this electrolyte at low temperatures is so poor that it is difficult to envisage that a fuel cell system would be rapidly

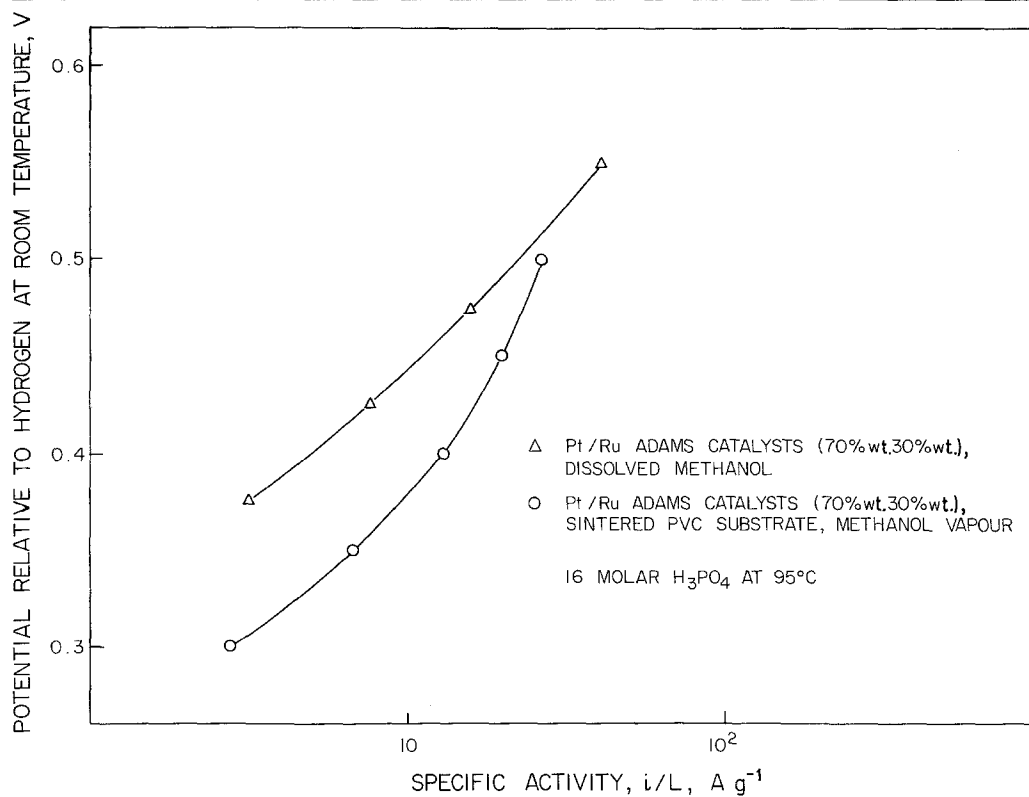


Fig. 11. Comparison of gas diffusion methanol electrode with dissolved methanol electrode.

self-warming from room temperature. Thus it would probably be more productive to concentrate on low temperature fuel cells (60° C or lower) where sulphuric acid is the preferred electrolyte of the two.

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