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Electrolytes for methanol-air fuel cells. II. The electro-oxidation of methanol in trifluoromethane-sulphonic acid monohydrate and aqueous solutions of trifluoromethane-sulphonic acid

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Trifluoromethanesulphonic acid monohydrate $CF_3SO_3H \cdot H_2O$ and its aqueous solutions have been evaluated as an electrolyte for methanol electro-oxidation. The performances of conventional noble metal catalysts in the pure monohydrate are very poor compared with those in 3 M sulphuric acid. This is contrary to previously published literature data, and possible reasons for the discrepancy are given. In aqueous solutions of CF_3SO_3H at concentrations between 10 and 50% wt. considerably improved performance is obtained and at 60° C the activities of the catalysts are in most cases slightly higher than in 3 M H_2SO_4. In addition the poisoning effect of acid radicals is considerably less in CF_3SO_3H than in H_2SO_4 solutions. Above 60° C, however, the aqueous $CF_3SO_3^-$ anion decomposes to produce sulphur, which poisons the noble metal catalysts.

Carbon-13 NMR studies of the $CF_3SO_3H/H_2O/CH_3OH$ system were carried out at 20 and 37° C. From the results it was concluded that no significant ester formation occurred between CH_3OH and $CF_3SO_3H \cdot H_2O$ at these temperatures. Earlier published data on ^1H NMR studies of these solutions had indicated that 100% of the methanol was involved in ester formation with the acid. A critical analysis of this ^1H NMR work is given.

Cyclic voltammetric characterization of catalysts in 10 and 25% wt. aqueous CF_3SO_3H solutions gave similar results to those in 3 M H_2SO_4; however, at concentrations of 50% wt. the acid decomposed at 0·0 V to produce a sulphur species that poisoned the catalyst.

The conclusion of the work was that while aqueous CF_3SO_3H solutions produced promising catalyst performance up to 60° C the slight improvement in performance over 3 M H_2SO_4 would not offset the greater expense of the CF_3SO_3H. In addition, it was suspected that the long-term stability of the aqueous solutions even at 60° C might be poor.

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1. Introduction

In Part I of this series [1] the relative merits of sulphuric and phosphoric acids as electrolytes for methanol electro-oxidation were discussed. A conclusion of that paper was that at low temperatures and low acid concentration sulphuric acid was the preferred electrolyte. However, it was quite clear that there existed with that electrolyte significant poisoning effects of the bisulphate anion and the undissociated sulphuric acid molecule. This, of course, results in the suppression of catalytic activity. Thus, it would be desirable to find an alternative acid electrolyte which did not exhibit large poisoning effects via adsorption of acid radicals. Such an acid, for application in a methanol–air fuel cell, would require in addition to have the following properties:

(1) Stability at fairly high temperatures in the event that a gaseous methanol–air system be chosen.

(2) A high ionic conductivity, i.e. strong acidity.

(3) A low vapour pressure at operating temperature.

(4) Low corrosivity towards the catalysts and materials used in the cell construction.

(5) The ability to dissolve the methanol and oxygen reactants.

Existing acid electrolytes do not meet these requirements. Sulphuric acid exhibits strong poisoning effects and is unstable at high temperatures. Phosphoric acid also exhibits poisoning effects and is a rather weak acid. Perchloric acid is much less poisonous to catalysts but is unstable at high temperatures.

Recently there has been some work on the application of perfluoroalkanesulphonic acids as electrolytes for hydrocarbon–air and hydrogen–air fuel cells [2–5]. In particular, trifluoromethanesulphonic acid monohydrate $CF_3SO_3H \cdot H_2O$ has been studied in some detail. It has been claimed that better catalyst performance is obtained in this acid than in phosphoric acid for both propane and hydrogen electro-oxidation [2–5]. Recently some work was also done on methanol electro-oxidation using $CF_3SO_3H \cdot H_2O$ as an electrolyte [4]. It was claimed that the electro-oxidation of methanol at a platinum foil catalyst at 80° C in $CF_3SO_3H \cdot H_2O$ produced higher activities than did a similar catalyst in 0·5 M H_2SO_4 at the same temperature. If these findings are indeed correct then this would have considerable implications for the development of methanol–air fuel cells.

Trifluoromethanesulphonic acid (CF_3SO_3H) or more trivially trifflic acid was discovered by Haszeldine and Kidd [6] who identified its resistance to thermal decomposition and hydrolysis. They were also able to show that it was one of the strongest protonic acids known. It is at least as fully ionized in water as is perchloric acid. The acid anion, like ClO_4^-, is a very weak complexing agent and as such might also be expected to have little poisoning effect on catalytic acitivity. The aqueous acid anion is kinetically stable in acidic solution up to 550 K [7]. The main reactions in its decomposition in aqueous acidic solution are [8]:

$$CF_3SO_3^- + 2H_2O \longrightarrow 3HF + HSO_4^- + CO \quad (1)$$

$$CF_3SO_3^- + 2H_2O + H^+ \longrightarrow 3HF + H_2SO_3 + CO_2 \quad (2)$$

$$3H_2SO_3 \longrightarrow 2HSO_4^- + S + H_2O + 2H^+. \quad (3)$$

It should be recognized that the products of its decomposition contain S and CO, which are potential poisons of Pt, and CO and SO_2 which are reducing agents. For instance, Fe^{3+} is reduced to Fe^{2+} in acidic aqueous trifflic acid solution at 470 K [9], and metals such as titanium and alloys such as stainless steel are attacked rapidly by aqueous trifflic acid at temperatures as low as 290 K [8], the reason for this being that the protective oxide coating on such materials is destroyed in the solution. Thus, in dealing with aqueous trifflic acid electrolytes we should be aware of its potential corrosivity.

It was decided, in the light of the relatively promising literature data on trifflic acid as a fuel cell electrolyte, to examine both the monohydrate and aqueous solutions thereof as electrolytes for methanol electro-oxidation. In this paper the performances of platinum foil, platinum electrodeposit, platinum Adams, 70% wt. platinum 30% wt. ruthenium Adams, platinum/tin electrodeposit and platinum/tin/lead electrodeposit have been evaluated. In addition, some characterization of the catalysts and electrolyte has been carried out.

2. Experimental

2.1. *Materials*

2.1.1. Trifluoromethanesulphonic acid (CF_3SO_3H). The acid was purchased (at a nominal purity of 97%) from Fluorochem Ltd. in 2 lb quantities at a cost of £84 per 2 lb batch. When received the acid was generally a colourless liquid although on occasions a fine precipitate (thought to be sulphur) was suspended in the liquid. Thus it was necessary to purify by distillation under nitrogen. Plastic tubing and teflon joints became discoloured during use and the distillation had to be conducted in a glass apparatus without using Teflon or grease in any of the joints. The fraction boiling at 164° C was collected and was a fuming colourless liquid.

2.1.2. Trifluoromethanesulphonic acid monohydrate ($CF_3SO_3H \cdot H_2O$). This was prepared initially in batches of 100 g by mixing equimolar quantities of the anhydrous acid and distilled water, pouring the water dropwise into the acid whilst cooling in an ice bath. The product was a white crystalline solid wetted by a clear liquid.

This product was distilled twice under nitrogen and the fraction boiling at 214–215° C was collected. The white crystalline product had a sharp melting point at 34° C in agreement with the results of other workers [2–5]. On preparation, the material generally supercooled to about 20° C at which temperature it crystallized after shaking.

2.1.3. Aqueous solutions of CF_3SO_3H. Aqueous solutions of CF_3SO_3H of concentration 50, 25 and 10% wt. were made up by simply adding the appropriate amount of distilled water to the monohydrate.

2.1.4. Sulphuric acid electrolyte. Analar H_2SO_4 was used without purification as the starting material. Solutions of 3 M (25% wt.) H_2SO_4 were made up by addition of distilled water.

2.1.5. Catalysts. (a) Platinum foil was cleaned by immersion in hot aqua regia followed by washing in distilled water. The dried foil was then heated to yellow heat prior to use.

(b) Platinum electrodeposits were prepared by potentiostatic deposition from chloroplatinic acid solution at + 0·050 V relative to the bubbling H_2 reference electrode. The substrates used were either etched Au foil or pyrographite coated carbon fibre paper.

(c) Pt/Sn and Pt/Sn/Pb electrodeposits were prepared as described previously [10] by potentiostatic deposition at 0·050 V from solutions of the appropriate salts on to Au foil or pyrographite-coated, carbon fibre paper.

(d) Platinum Adams and 70% wt. Pt 30% wt. Ru Adams were used as received from Johnson Matthey Co. The electrodes were prepared by spraying a slurry of the catalyst with 1% wt. low-density polyethylene in carbon tetrachloride onto either Au foil or pyrographite-coated carbon fibre paper. The catalysts were ionically bombarded at an air pressure of 0·2 mm Hg for 15 min to make the surface hydrophilic.

2.2. *Electrochemical measurements*

2.2.1. Catalytic activity. Polarization curves were measured galvanostatically at temperatures between 25 and 90° C using a PAR model 173 potentiostat/galvanostat. The concentration of methanol in the electrolyte was constant at 1 M. From 25–60° C it was possible to carry out the experiments in a conventional three-armed cell incorporating a bubbling H_2 reference electrode. However, from 60–90° C some problems were encountered in the aqueous solutions of trifflic acid owing to the decomposition of the electrolyte in the reference electrode compartment. In this temperature range either a three-armed cell with an external bubbling H_2 reference electrode (separated from the cell by a multi-bridge system) or a two-armed cell with an external $Hg/HgSO_4$ reference electrode was used. Corrections were made for both junction potential and temperature difference of the reference. The counter electrode was either a platinum gauze or a spectroscopically pure graphite rod. The catalyst was usually cathodized in 3 M H_2SO_4 then cycled poteniostatically to potentials of 0·5 V to give a clean metal surface prior to transfer to the cell containing the trifflic acid solution.

The performance of the catalyst is presented as Tafel plots of potential relative to the bubbling H_2 reference versus specific activity–specific activity being defined as the number of $A\,g^{-1}$ of platinum in the catalyst.

2.2.2. Cyclic voltammetry. Cyclic voltammograms were measured using a PAR 173 potentiostat and a PAR model 175 Universal Programmer in conjunction with a Bryans X–Y recorder. The cycling programme was generally carried out between 0 and 1·6 V at a sweep speed of 50 mV s^{-1} in 3 M (25% wt.) H_2SO_4 and in different concentrations of trifflic acid.

2.3. *Carbon-13 nuclear magnetic resonance*

To check on the extent of ester formation between methanol and trifflic acid some carbon-13 NMR spectra were recorded at 20·0 MHz on a Varian Associates CFT-20 NMR Spectrometer operating in the Fourier transform mode. Samples were diluted with sufficient D_2O (approximately 10%) to provide a ^2H field frequency lock. Spectra were obtained with proton noise decoupling, using sequences of 30° pulses (7 μs) and an acquisition time of 1·023 s. Signal to noise was improved by multiplication of the Free Induction Decay (FID) by an exponential function of time constant

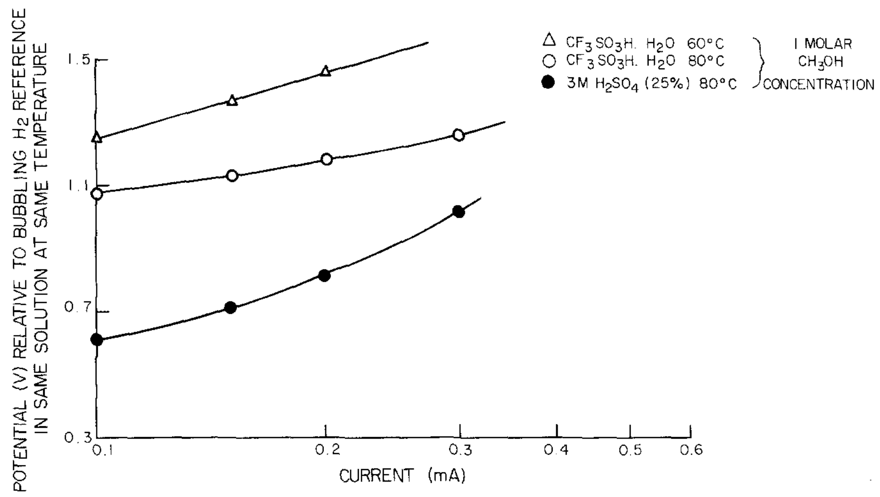

Fig. 1. Performance of Pt foil catalyst for the electro-oxidation of methanol in $CF_3SO_3H.H_2O$.

0·15–0·20 s. (Spectral widths of 4000 Hz were generally employed giving 0·98 Hz/point.)

3. Results and discussion

3.1. *Catalytic activity measurements*

3.1.1. $CF_3SO_3H.H_2O$. The performance of platinum foil catalyst in $CF_3SO_3H.H_2O$ is compared with that in 3 M H_2SO_4 at 80° C in Fig. 1. The activity in $CF_3SO_3H.H_2O$ is some 250–350 mV poorer than in 3 M H_2SO_4, the upper and lower limits depending on the potential at which the comparison is made. This is contrary to the reported data of Adams and Foley [4] who claimed that the activity of platinum foil in $CF_3SO_3H.H_2O$ at 80° C was superior to that in 0·5 M H_2SO_4. The results of Adams and Foley were presented as curves of potential versus current produced per real square centimetre of platinum surface and they compared their results with those of Bagotsky and Vassilyev [11] in 0·5 M H_2SO_4. Our results are quoted simply as the number of milliamps produced rather than as current densities, since the same electrode was used in both electrolytes and we were only looking for comparisons between electrolytes. The only explanation which would account for this

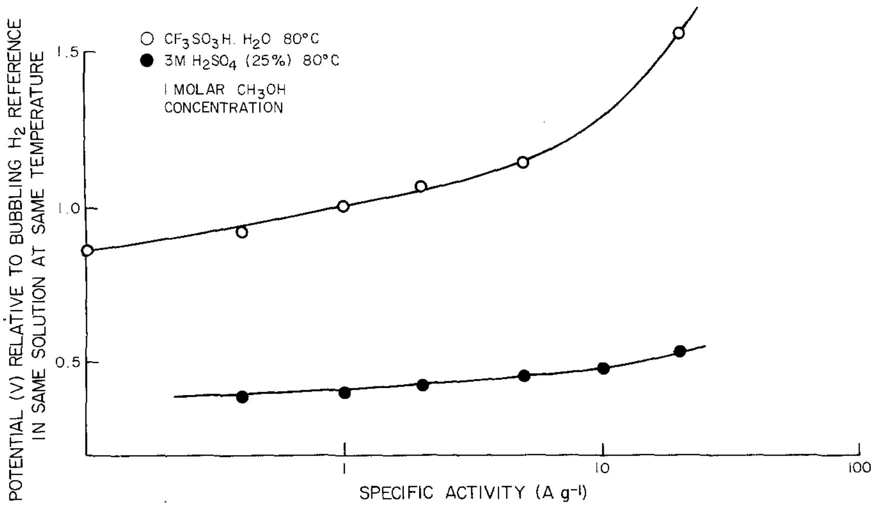

Fig. 2. Performance of Pt Adams catalyst for the electro-oxidation of methanol in $CF_3SO_3H.H_2O$.

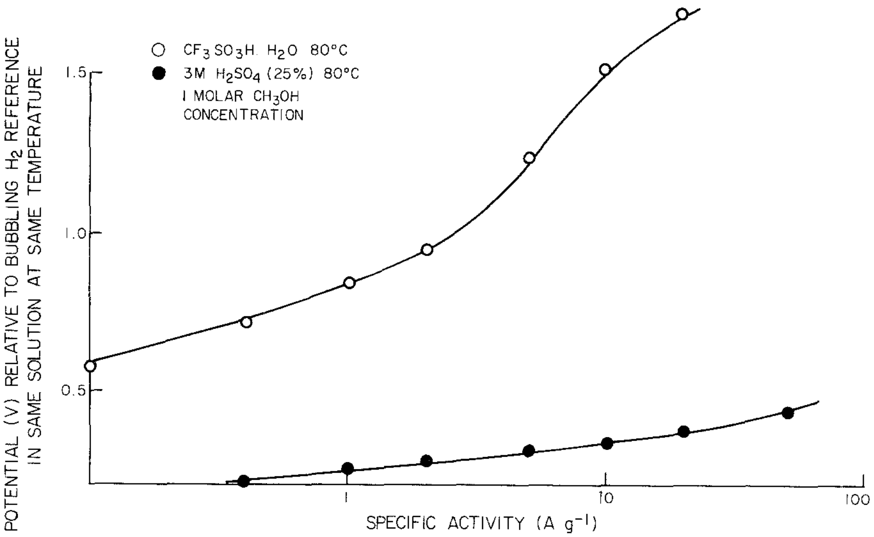

Fig. 3. Performance of 70% wt. Pt 30% wt. Ru Adams catalyst for the electro-oxidation of methanol in $CF_3SO_3H \cdot H_2O$.

discrepancy would be errors in the metal surface area measurements used by either Adams and Foley, or Bagotsky and Vassilyev but a large error would be involved. Certainly our results seem to make sense since it is expected that methanol electro-oxidation in an electrolyte such as $CF_3SO_3H \cdot H_2O$ should be less facile than in 0·5 M or 3 M H_2SO_4 since the water activity of the fluorosulphonic acid monohydrate is so much lower.

The findings with platinum foil that $CF_3SO_3H \cdot H_2O$ gives rise to poorer performance than 3 M H_2SO_4 were confirmed by tests on more realistic, finely divided catalysts. The performances of Pt Adams and 70% wt. Pt 30% wt. Ru Adams catalysts are shown in Figs. 2 and 3, where the inferior performance in trifflic acid monohydrate can be seen. We found also that at temperatures higher than 80° C the activities of the catalysts decreased. A possible reason for this was decomposition of the electrolyte producing S species which could poison the catalyst. However, cyclic voltammetry studies showed no evidence of sulphur poisoning of the catalysts (Fig. 4). Thus, for the moment the reason for the fall-off in performance above 80° C remains unclear.

3.1.2. Aqueous solutions of CF_3SO_3H. In the light of the results with $CF_3SO_3H \cdot H_2O$ it was decided

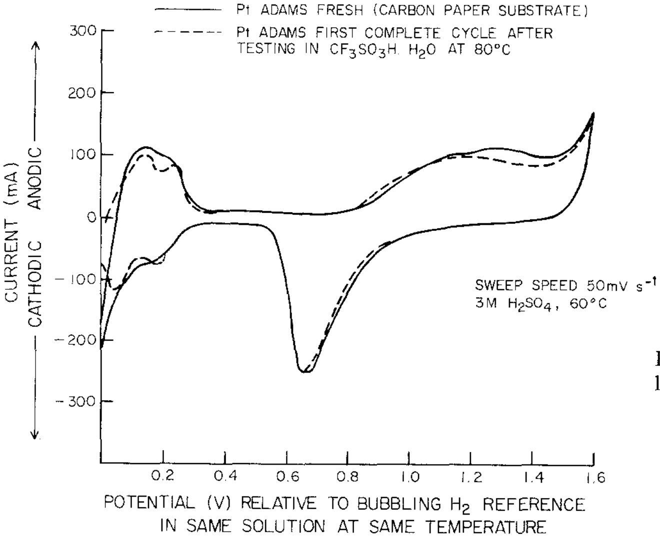

Fig. 4. Cyclic voltammograms of Pt Adams catalyst after testing at 80° C in $CF_3SO_3H \cdot H_2O$.

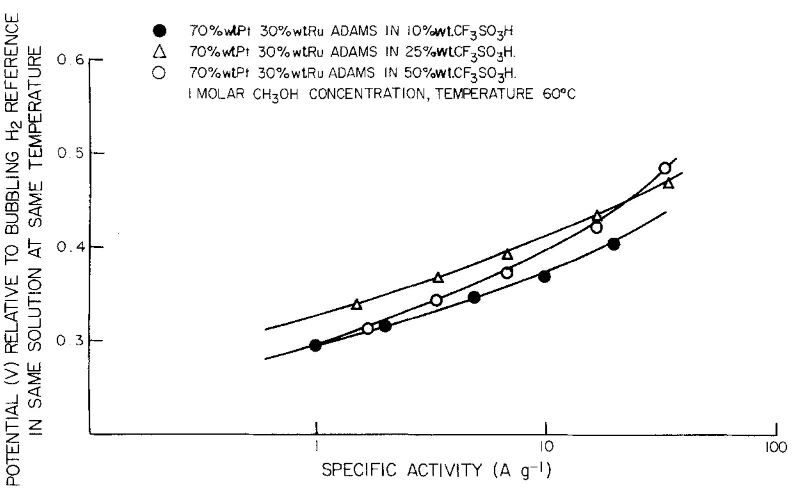

Fig. 5. Influence of trifflic acid concentration on the performance of the catalyst.

to look at aqueous solutions of the electrolyte to determine whether more realistic currents could be obtained and solutions of 10, 25 and 50% wt. CF_3SO_3H were studied at temperatures between 25 and 90° C. Results obtained using either the multi-bridged hydrogen reference experimental apparatus or the single-bridge Hg/HgSO$_4$ reference apparatus were reproducible and so no reference to the particular apparatus used will be made in the discussion of the results.

It has been suggested in the introduction that because of the weaker complexing nature of the aqueous $CF_3SO_3^-$ anion the concentration of acid should not have such a marked effect on the performance of the catalysts since poisoning effects should be minimal. The performance of 70% wt. Pt 30% wt. Ru Adams catalyst in 10, 25 and 50% wt. CF_3SO_3H is therefore shown in Fig. 5. For comparison the performance of a similar catalyst in a wide range of concentrations of H_2SO_4 is shown in Fig. 6. The influence of acid concentration is seen to be quite marked over the whole concentration range for H_2SO_4 indicating that the poisoning effect of adsorbed acid radicals is quite marked for that electrolyte. Similar results were found previously with H_3PO_4 electrolyte [1]. However, for trifflic acid while large improvements in performance were observed between

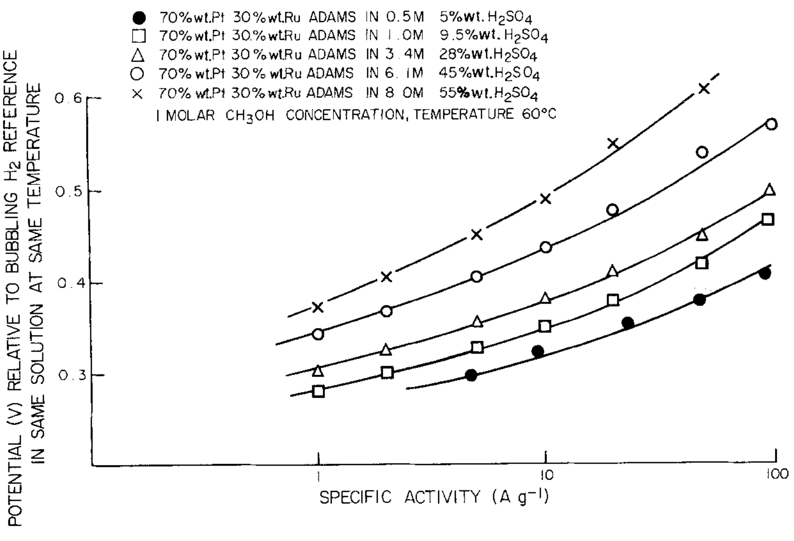

Fig. 6. Influence of sulphuric acid concentration on the performance of the catalyst.

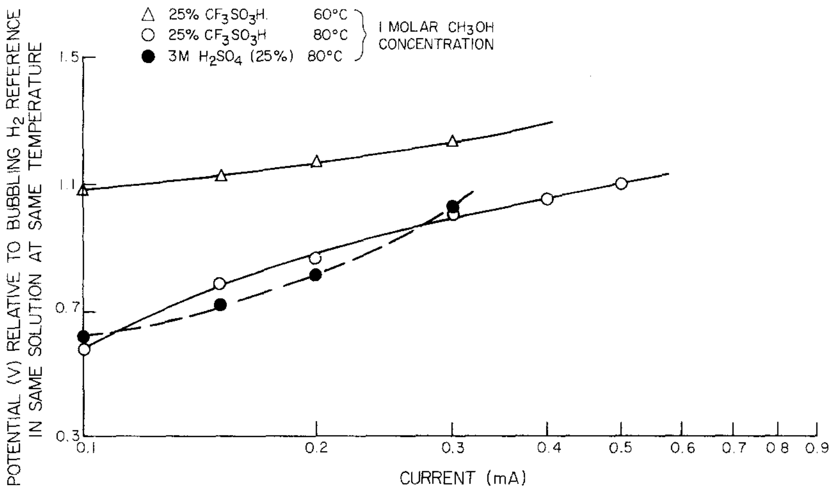

Fig. 7. Performance of Pt foil catalyst for the electro-oxidation of methanol in 25% wt. CF_3SO_3H aqueous solution.

$CF_3SO_3H \cdot H_2O$ and 50% wt. CF_3SO_3H the performance did not vary in any regular fashion between 10 and 50% wt. These results indicate that while significantly more water is required for reaction than exists in $CF_3SO_3H \cdot H_2O$, there is little influence of adsorption of $CF_3SO_3^-$ anion between 10 and 50% wt. concentrations. This can be rationalized, as mentioned above, in regard to the weak complexing nature of the $CF_3SO_3^-$ anion.

A more detailed study of the catalysts' performance in aqueous trifflic acid was made at an acid concentration of 25% wt. The activities of Pt foil, Pt Adams, 70% wt. Pt 30% wt. Ru Adams, Pt/Sn and Pt/Sn/Pb catalysts were measured in this electrolyte and compared with the performance in 3 M H_2SO_4 (25% wt.). The measurements were carried out at 25, 35, 45, 60 and in some cases 80 and 90°C. The results are shown in Figs. 7–11. The activities in this electrolyte, at all temperatures up to 60° C, were better than or equal to that in 3 M H_2SO_4 at the same temperatures although at 60° C the improvements were only marginal. The improved performance could be attributed to the smaller poisoning effect of the trifflic acid anion; however, more data on vapour pressure and water activity of the trifflic acid solutions are required

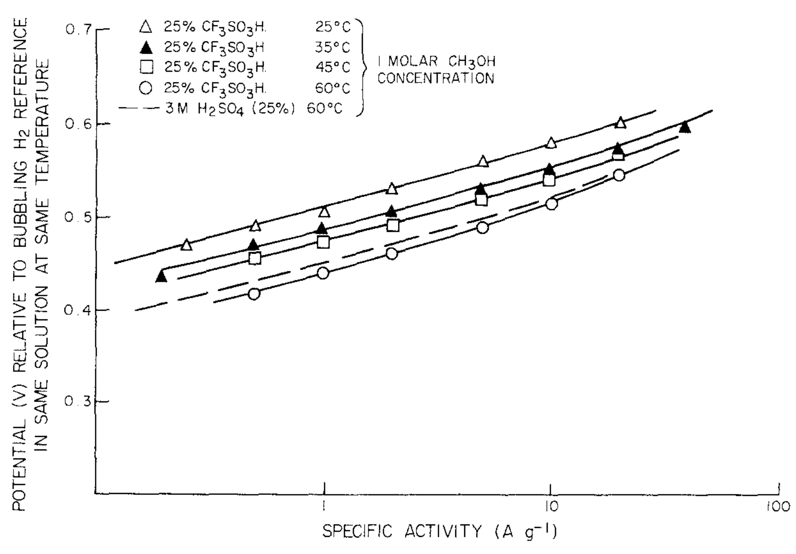

Fig. 8. Performance of Pt Adams catalyst for the electro-oxidation of methanol in 25% wt. CF_3SO_3H aqueous solution.

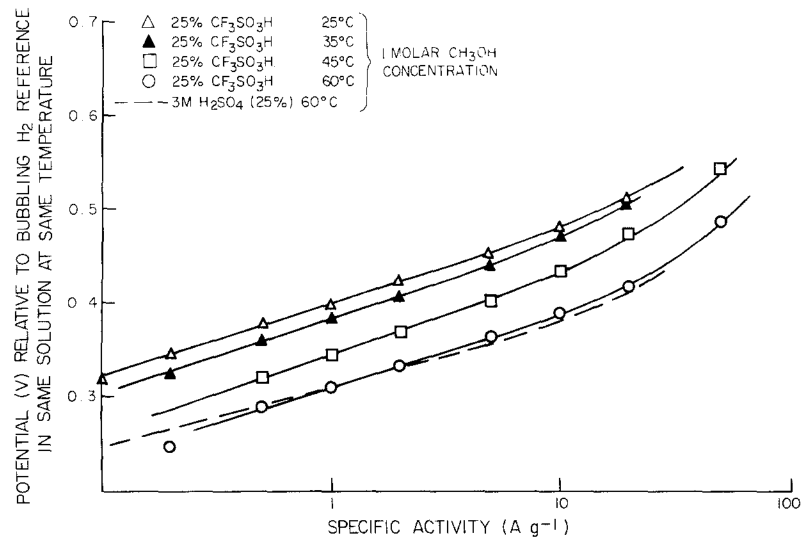

Fig. 9. Performance of 70% wt. Pt 30% wt. Ru Adams catalyst for the electro-oxidation of methanol in 25% wt. CF_3SO_3H aqueous solution.

before a definite conclusion can be reached. Arrhenius plots of catalytic activity (in A g^{-1}) at a fixed potential versus $1/T$ led to values of the activation energy for each catalyst. The values found are collected along with the Tafel slopes for each catalyst in Table 1. The Tafel slopes are marginally higher in 25% wt. CF_3SO_3H than in 3 M (25% wt.) H_2SO_4 whilst the activation energies are between 2 and 5 kcal mol^{-1} lower than in 3 M H_2SO_4. These results could imply the operation of a different electro-oxidation mechanism in aqueous CF_3SO_3H from that operative in H_2SO_4. Alternatively, the higher activation energies found for H_2SO_4 may simply reflect a smaller poisoning effect of the acid radicals as the temperature is increased. The low activation energies found in aqueous trifflic acid mean that smaller bonuses are obtained by increasing the temperature than are found with H_2SO_4.

It was observed that on going to temperatures

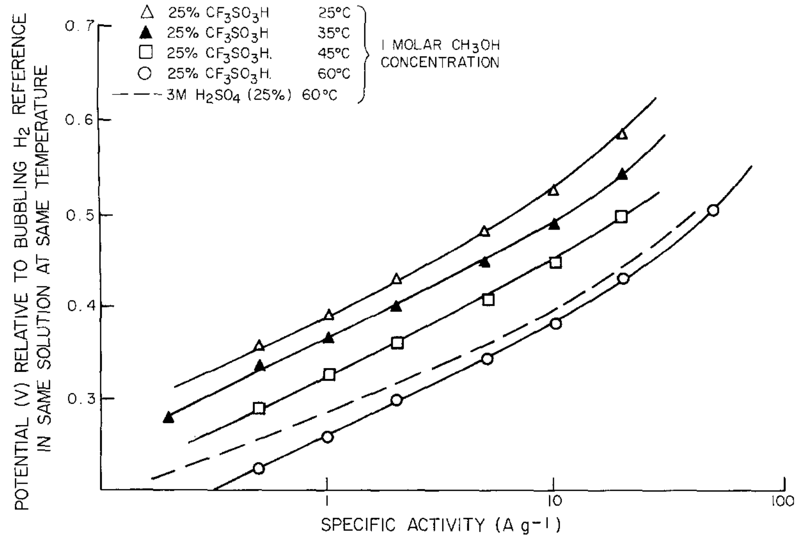

Fig. 10. Performance of Pt/Sn electrodeposited catalyst for the electro-oxidation of methanol in 25% wt. CF_3SO_3H aqueous solution.

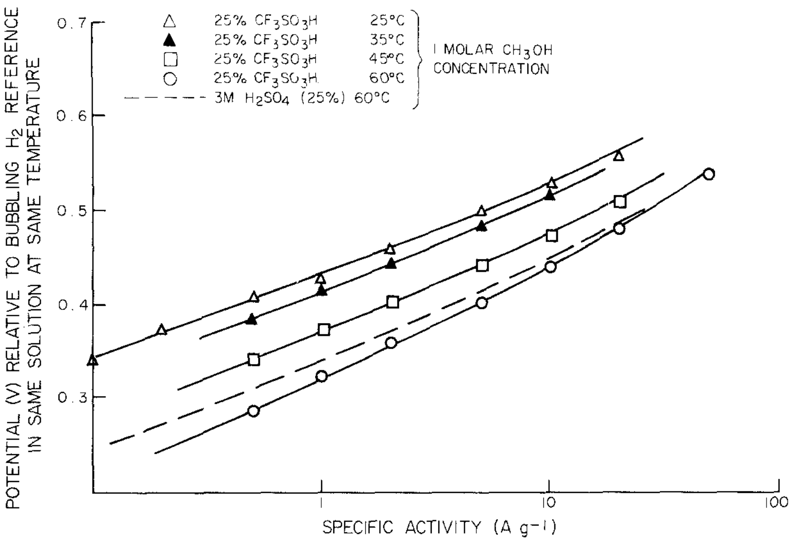

Fig. 11. Performance of Pt/Sn/Pb electrodeposited catalyst for the electro-oxidation of methanol in 25% wt. CF_3SO_3H aqueous solution.

higher than 60° C that the activity decreased with temperature at all the concentrations studied. This coincided with a strong smell of hydrogen sulphide from both working and counter electrode compartments of the cell. A cyclic voltammetric study of the catalysts after testing at this temperature revealed considerable poisoning of the noble metal catalyst by a sulphur species. The voltammetric profile of a fresh Pt Adams catalyst and of a poisoned Pt Adams catalyst are shown in Fig. 12. For the sample poisoned after testing at 80° C the metal surface area as calculated from the H desorption area (assuming $210\,\mu C\,cm^{-2}$ metal area) is considerably reduced and a new peak on the anodic sweep appears at 1·3–1·4 V. This could be due to delayed formation of platinum oxides; however, the number of coulombs passed in this region is greater than that passed during oxide reduction on the cathodic sweep and so it seems that some other origin of the peak at 1·3–1·4 V must be sought. Much work has been done on the potentiodynamic cycling of platinum catalysts in the presence of small concentrations of H_2S in H_2SO_4 [12–14] and it has been reported [13] that several processes can occur, one of which gives a peak on the anodic sweep at 1·42 V attributed to the oxidation of H_2S giving sulphur as the main product. As a result of this either the electrode is covered with a layer of elemental sulphur or a platinum sulphide is formed. The platinum sulphide is oxidized in the following reaction:

$$PtS + 4H_2O \longrightarrow PtO_2 + SO_2 + 8H^+ + 8e$$

and the peak at 1·3–1·4 V is accounted for by this reaction. On the cathodic sweep the PtO_2 is reduced:

Table 1. Comparison of Tafel slopes and activation energies in 25% wt., CF_3SO_3H./1 M CH_3OH and 3 M (25% wt.) H_2SO_4/1 M CH_3OH

Catalyst	*Tafel slope at* 60° C (mV dec⁻¹)		*Activation energy at* 25–60° C (kcal mol⁻¹)	
	H_2SO_4	CF_3SO_3H	H_2SO_4	CF_3SO_3H
Pt (Adams)	65	70	15·9	11·1
70% wt. Pt 30% wt. Ru (Adams)	65	80	19·0	16·1
Pt/Sn electrodeposit	105	120	16·4	14·7
Pt/Sn/Pb electrodeposit	105	115	19·2	14·3

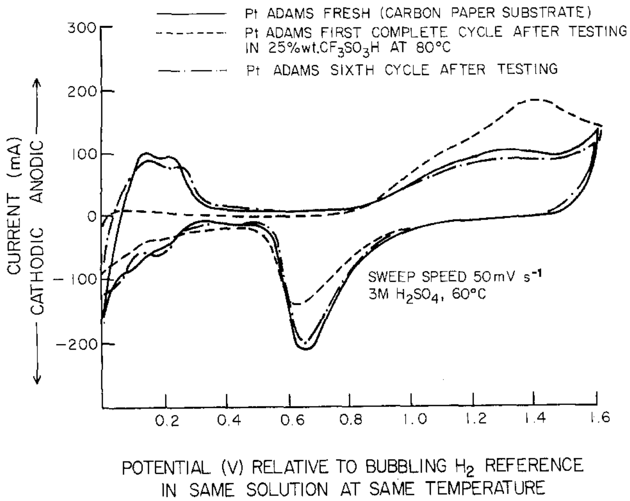

Fig. 12. Cyclic voltammograms of Pt Adams catalyst after testing at 80° C in 25% wt. CF_3SO_3H.

$$PtO_2 + 4H^+ + 4e \longrightarrow Pt + 2H_2O$$

accounting for the characteristic peak at 0·7–0·75 V. Subsequent cycling shows that the peak at 1·3–1·4 V diminishes in intensity concomitantly with the rise in intensity of the H_2 adsorption/desorption and Pt oxide reduction peaks until the profile is identical with that of a fresh unpoisoned catalyst. The source of the sulphur and hence platinum sulphide on the catalyst during the activity tests at above 60° C would seem to be the decomposition of the electrolyte in either or both of the counter and working electrode compartments of the cell.

Aqueous $CF_3SO_3^-$ anion, as mentioned previously, is reported to be stable in an acidic solution up to about 550 K but the stability is kinetic rather than thermodynamic [8]. Thus, at temperatures above 60° C (333 K), it is possible that at both working and counter electrodes in our test cell, the decomposition of the anion might be catalysed – in the working compartment by the finely divided working electrode catalyst or in the counter electrode compartment by either the H_2-covered platinum or the graphite counter electrode. In addition, the role of methanol itself in the decomposition of the acid may be significant. The products of the decomposition are all potential poisons for the noble metal working electrode catalyst. Decomposition can occur by either

$$CF_3SO_3^- + 2H_2O \longrightarrow 3HF + HSO_4^- + CO \quad (4)$$

or

$$CF_3SO_3^- + 2H_2O + H^+ \longrightarrow 3HF + H_2SO_3 + CO_2. \quad (5)$$

After Reaction 5 disproportionation of H_2SO_3 can occur

$$3H_2SO_3 \longrightarrow 2HSO_4^- + S + H_2O + 2H^+ \quad (6)$$

From the voltammograms it is clear that S is the poison involved so presumably at least Reactions 5 and 6 occur leading to poisoning by adsorbed sulphur. The formation of H_2SO_3 can also occur in dilute H_2SO_4 solutions but we have not noticed this effect below 100° C.

If Reaction 5 is rate limiting then the rate of formation of S should be proportional to $[CF_3SO_3H]\,[H_2O]^2$. If we plot this relationship (Fig. 13) then it can be seen that a maximum in decomposition rate occurs at about 33% wt. acid concentration. We have studied 25 and 50% wt. concentrations which are on opposite sides of the maximum and indeed we find considerable S poisoning above 60° C. However, with the monohydrate, which from Fig. 13 should show a much lower decomposition rate, we found no evidence of S poisoning up to 90° C. Thus, it could be concluded on the basis of this hypothesis that the S poisoning problem could be minimized by a careful selection of the concentration of aqueous CF_3SO_3H. Concentrations of say $< 10\%$ wt. or $> 90\%$ wt. might be of interest. However, we feel that with concentrations $< 10\%$ wt. problems

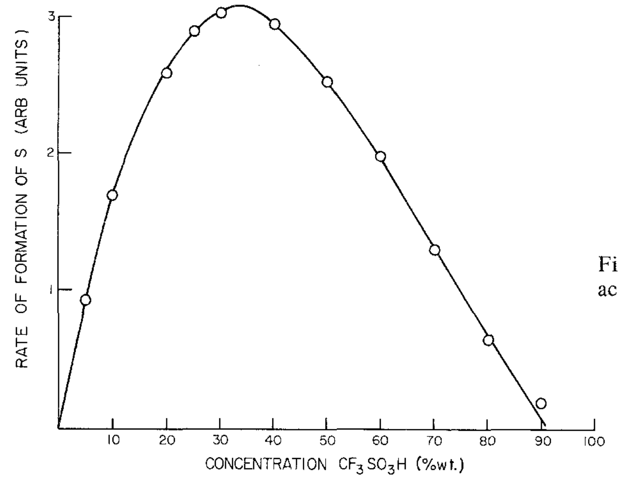

Fig. 13. Dependence of rate of formation of S on trifflic acid concentration.

would arise in a complete fuel cell because of the high partial pressure of water vapour whilst with a concentration of > 90% wt. the water activity would probably be too low to produce significant activity.

3.2. *Cyclic voltammetry studies in aqueous CF_3SO_3H*

Cyclic voltammetry measurements were made at 25° C in different concentrations of CF_3SO_3H. Typical profiles of platinum electrodeposit and platinum Adams catalysts in 25% wt. CF_3SO_3H are shown in Figs. 14 and 15 where a comparison is made with the profiles in 3 M (25% wt.) H_2SO_4. While the peak position for the various processes such as H_2 adsorption/desorption, Pt oxide formation and reduction are not identical for both electrolytes, the general forms of the voltammograms are similar. The metal surface areas calculated from the H_2 desorption region of the profiles in the two electrolytes are very similar, However, when the profiles of the same catalysts were measured in 50% wt. CF_3SO_3H considerable differences between the profile were observed (Fig. 16). The metal surface area of a Pt electrodeposit was considerably reduced. A new peak on the anodic sweep occurs at 1·3–1·4 V. By analogy with the sulphur poisoning work described in Section 3.1.2, it seems that this peak arises from the oxidation of a sulphur species adsorbed on the Pt surface. This would account for the lower metal surface areas found. It seems likely that the poisoning sulphur species arises from reductive decomposition of the electrolyte at the working electrode at 0·0 V at the beginning of the cycling programme.

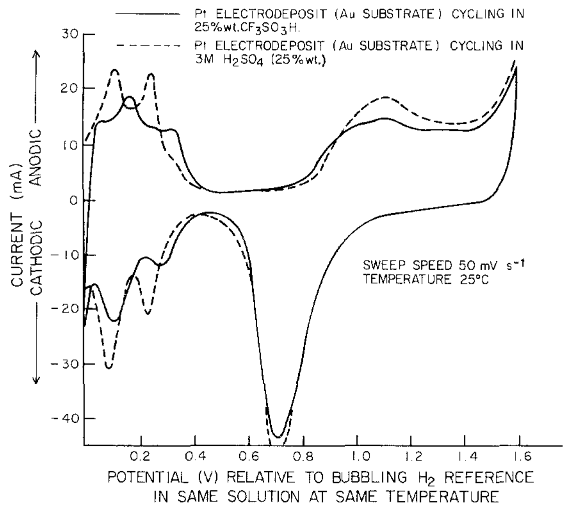

Fig. 14. Comparison of voltammetric profiles of Pt electrodeposited catalyst in 25% wt. CF_3SO_3H and 3 M H_2SO_4 (25% wt.).

A platinum electrodeposit poisoned by extensive cycling in 50% wt. CF_3SO_3H was cycled in 3 M H_2SO_4. On the first cycle (Fig. 17) the peak arising from removal of the poisoning S species is apparent at 1·3–1·4 V and the H_2 adsorption/desorption peaks and Pt oxide reduction peaks are greatly diminished. However, with continued cycling the profile gradually reverts to that which is typical for a fresh platinum electrodeposit.

It is thus apparent from these results that for adequate characterization of catalyst surfaces in

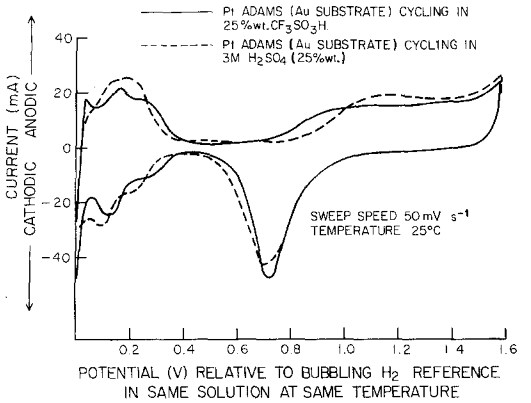

Fig. 15. Comparison of voltammetric profiles of Pt Adams catalyst in 25% wt. CF_3SO_3H and 3 M H_2SO_4 (25% wt.).

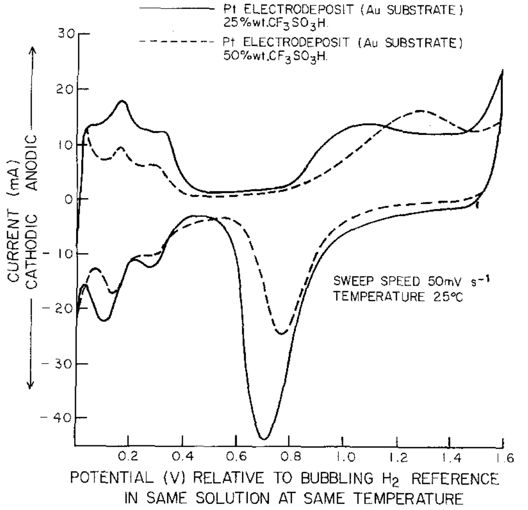

Fig. 16. Influence of CF_3SO_3H concentration on voltammetric profile.

aqueous CF_3SO_3H using cyclic voltammetry the measurements must be confined to low or very high concentrations of CF_3SO_3H (cf. Fig. 13).

3.3. *Carbon-13 NMR*

The $CF_3SO_3H/H_2O/CH_3OH$ system was investigated to determine the extent of possible ester ($CF_3SO_3CH_3$) formation using carbon-13 NMR spectroscopy. Carbon-13 NMR spectra of two samples (1 M CH_3OH dissolved in $CF_3SO_3H \cdot H_2O$ and 10% wt. aqueous CF_3SO_3H respectively, containing approximately 10% wt. D_2O in each case) at 37° C showed resonances corresponding to both CF_3SO_3H and CH_3OH, with no evidence of the ester methyl resonance (expected 10–25 ppm to low field of the alcohol resonance). The concentration of the ester, if present, must therefore be < 5 mol % of that of the alcohol, estimated from the signal/noise available. Similar results were also obtained at 20° C.

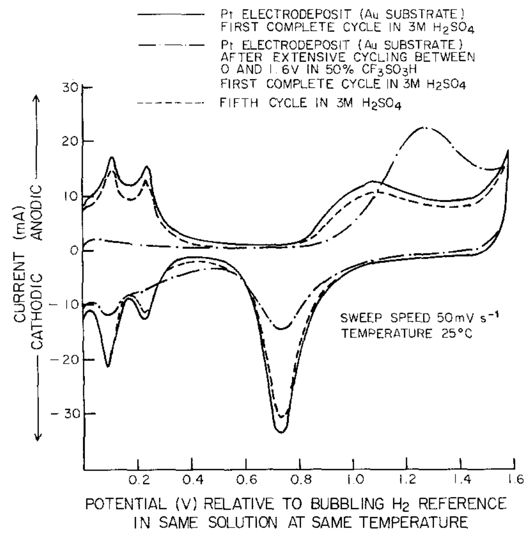

Fig. 17. Cyclic voltammograms of Pt electrodeposit in 3 M H_2SO_4 after poisoning in 50% CF_3SO_3H.

Successive addition of D_2O to a solution of CH_3OH (approximately 4 M) in $CF_3SO_3H \cdot H_2O$ gave samples containing, 10, 20 and 40% wt. D_2O. Each of these was studied at 20° C and again no evidence for the ester was seen in any case. This indicates that the ester, if present, must be at a concentration of less than 3 mol %. The existence of an alcohol–ester equilibrium, fast, on the NMR timescale, is considered unlikely because of the relatively small shifts seen in the CH_3OH resonance as the concentration of D_2O increases.

These results seemed rather surprising since the earlier proton NMR work of Adams and Foley [4] indicated that 100% esterification occurred. Their results were based on the observation of only one discrete singlet in the methyl region of the ^1H NMR spectra of $CH_3OH/CF_3SO_3H \cdot H_2O$ solutions.This singlet appeared 0·644 ppm downfield of the signal seen for the CH_3OH ^1H NMR methyl singlet. This difference however is not significant having regard to the facts that (a) the spectrum of $CF_3SO_3H \cdot H_2O + CH_3OH$ was recorded with an external TMS capillary for reference, and is therefore not corrected for bulk susceptibility variations between the two samples; (the condition for measurement of the CH_3OH sample is not reported; if similarly recorded, the errors must still be appreciable) and (b) the solution of CH_3OH in a strong acid such as trifflic acid must cause shielding variations due to hydrogen bonding and protonation–deprotonation effects. In summary, it would have been a considerable coincidence had the methanol resonances been coincident; the 0·644 ppm (38 Hz) variation is not considered excessive, and the two observed resonances are both probably due to CH_3OH species modified by bulk susceptibility and solvent effects.

4. Conclusions

Trifluoremethanesulphonic acid monohydrate $CF_3SO_3H \cdot H_2O$, contrary to previously published data [4], is not an attractive electrolyte for methanol electro-oxidation. Catalytic activities in $CF_3SO_3H \cdot H_2O$ were very low compared with those in 3 M (25% wt.) H_2SO_4. The reason for the low activity seems to be the low water activity of the monohydrate. If comparisons were made with highly concentrated H_2SO_4 and H_3PO_4 then the differences in activity would be smaller, but concentrated H_2SO_4 and H_3PO_4 are also very poor electrolytes for methanol electro-oxidation. The reason for the somewhat high activities found in the monohydrate by earlier workers [4] compared with those in 0·5 M H_2SO_4 is not established. A possibility is that there may be some uncertainties in the surface areas of the Pt foils used in that work.

Above about 80° C the performance in $CF_3SO_3H \cdot H_2O$ deteriorates with increasing temperature. The reason for this has not been established since no evidence of sulphur poisoning was found. Possibly some interaction between methanol and trifflic acid monohydrate takes place at these temperatures. Analytical studies of the electrolyte solution at these temperatures might throw some light on this problem.

Aqueous solutions of CF_3SO_3H between 10 and 50% wt. showed promising performances at temperatures between 25 and 60° C. The poisoning effect of acid radicals was not so marked as with other acids such as H_2SO_4 and H_3PO_4. However, above about 60° C a fall-off in catalytic activity was observed and evidence was found for sulphur poisoning of the catalysts at these temperatures. This arises probably from decomposition of the aqueous acid anion.

Carbon-13 NMR studies revealed no evidence of methyl ester formation in concentrated and dilute solutions of CF_3SO_3H, H_2O and CH_3OH. This refutes earlier claims [4] that all of the methanol in such solutions existed as the methyl ester of trifflic acid. A critical analysis of the original ^1H NMR results has been given in explanation.

Characterization of catalysts by cyclic voltammetry in trifflic acid at concentrations up to 25% wt. gave similar results to conventional characterization in H_2SO_4. However, at concentrations of 50% wt. problems were encountered with the decomposition of the acid leading to sulphur poisoning of the noble metal.

In conclusion, it can be said that while aqueous trifflic acid does produce good performance for typical methanol electro-oxidation catalysts there is no marked advantage over conventional electrolytes such as H_2SO_4. In a commercial sense any gains arising from the slightly higher activity in aqueous CF_3SO_3H at 60° C would be offset by the increased cost of acid. In addition the long-term stability of aqueous trifflic acid solutions at this temperature is uncertain. At higher temperatures the susceptibility of the aqueous acid anion to decomposition rules out its application.

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