Direct Methanol Fuel Cells

RECENT DEVELOPMENTS IN THE SEARCH FOR IMPROVED PERFORMANCE

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Unlike other fuel cell types, the direct methanol fuel cell does not require a separate hydrogen generation system and therefore has greater commercial potential, particularly for powering portable appliances. However, the limiting factor for the cost-effective performance of such systems is the catalytic activity of the electrodes, in particular the anode. The single most active anode material is platinum, which is usually dispersed on a high surface area carbon support. It has been found that the addition of small amounts of metals such as lead, rhenium, ruthenium and tin to the platinum produces a significant increase in activity. The best of these bimetallic systems is based on a mixture of platinum and ruthenium. However, further worthwhile improvements in anode activity could result from a more fundamental understanding of the methanol decomposition reaction. In recognition of this, the Commission of the European Communities has initiated a research programme which involves collaboration between universities and industry in four member states. This article is based largely upon a paper given at the CEC–Italian Fuel Cell Workshop in Taormina, Sicily, in June 1987.

Fuel cells convert chemical energy to direct current electrical energy without intermediate steps (1). Most fuel cells are powered by hydrogen and oxygen (air) which on combining give water as a by-product. However, the direct methanol fuel cell (DMFC) functions by oxidising the liquid fuel to carbon dioxide and water. This removes the need for an external hydrogen fuel supply and offers the prospect of producing compact systems ranging in size from a few watts up to several kilowatts. The potential market for DMFCs is both as an alternative to storage batteries and also as an independent power generator where higher output is required. Probable applications include use in video cameras and recorders, and in boats and caravans, where in many cases batteries can only be used for short operating periods before recharging is required, whereas fuel cells are capable of continuous operation provided that they are supplied with fuel. DMFCs have the double advantage of using a relatively safe liquid fuel at a low operating temperature, and in the longer term they could find application as alternative power sources for vehicle propulsion.

The possibility of using fuels such as alcohols and aldehydes in fuel cells was first recognised by Kordesch in 1951 (2), although serious investigations did not commence until the early 1960s. Methanol has attracted most interest as a fuel because it is inexpensive, widely available and can be handled and distributed to the consumer very easily. The DFMC can operate using either acid or alkaline electrolytes, and both of these systems have been studied extensively over the last 25 years, notably by Shell and Esso. In the period 1960 to 1970 Esso Research and Engineering worked under contract to the U.S. Army (3) to develop a 100 watt system for use in military equipment, in response to a requirement for a lightweight

Fig. 1 Many of the potential applications of direct methanol fuel cells are in domestic and leisure markets. Hitachi have constructed a golf cart with a direct methanol fuel cell in a hybrid system alongside a lead acid battery

power source for use in communications equipment. The initial unit developed by Esso gave 55 mA/cm² at 0.4V, using noble metal electrocatalysts, but durability was limited. Shell produced a prototype 40 cell, 300 watt stack in 1963 (4), and later extended their studies to develop the DMFC for automotive power applications (5–9). Shell studied methanol oxidation (anode) catalysts extensively and found that a platinum/ruthenium system was among the most active of the ones tested, although it did not meet their activity target. Both Shell and Esso terminated this research and development in the late 1970s, because the catalytic activity which had been developed for methanol oxidation was insufficient for effective commercialisation. Other DMFC systems have been investigated by Cathro and Weeks (10), Brown Boveri (11), the U.S. Army for military communication systems (12–14) and the Royal Institute of Technology, Stockholm, for electric wheelchairs (15, 16).

More recently, Hitachi has reopened investigations into acid electrolyte DMFCs (17) and interest in these power sources has been rekindled. Hitachi foresee the applications as being mainly in the leisure and domestic markets, initially as lightweight hybrid systems

used in conjunction with lead acid batteries, for example in golf carts, as shown in Figure 1 (18). In their systems, Hitachi have generally used platinum as the cathode catalyst and a combination of platinum and ruthenium in the anode.
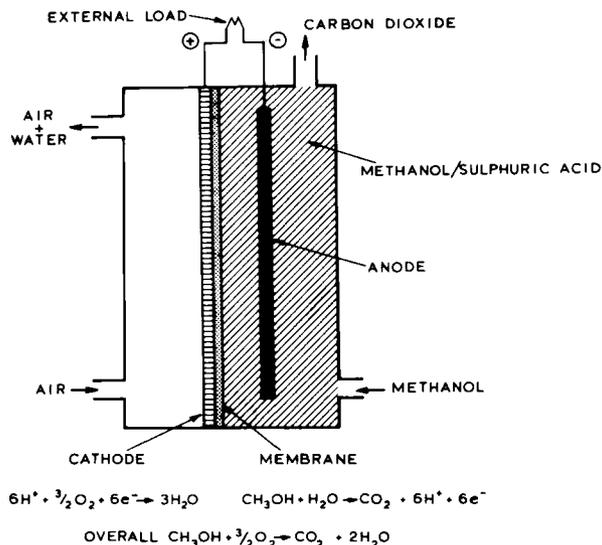
As noted earlier, direct methanol fuel cells can be designed to operate either in acid or alkaline electrolyte. Ideally, a good electrolyte should have high ionic conductivity, produce no corrosion of the cell or catalyst materials and cause no poisoning effects or detrimental side reactions. In this context, alkaline electrolytes offer superior electrochemical performance and improved fuel cell output, compared to acid systems. However, the seemingly intractable problem of carbonate build-up in cells with alkaline electrolyte, due to the reaction:

$$CO_2 + OH^- = HCO_3^-$$
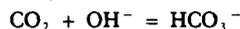
has so far precluded their commercialisation. Consequently most research has focused on acid electrolyte systems.

A schematic representation of an acid electrolyte DMFC, together with the principal reactions involved, is shown in Figure 2. A methanol molecule reacts with a water molecule at the anode liberating carbon dioxide, 6 protons and 6 electrons—a very high electron yield. The carbon dioxide produced in the reaction is

Fig. 2 In the direct methanol fuel cell, methanol reacts with water at the anode and oxygen is reduced at the cathode. Carbon dioxide and water are the reaction products

$6H^+ + \frac{3}{2}O_2 + 6e^- \rightarrow 3H_2O$ $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

OVERALL $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$

rejected by the acid electrolyte. Oxygen is reduced at the cathode, producing water, which is removed by the air flowing through the cathode compartment. The maximum voltage attainable from the overall reaction in the methanol–air cell is in theory 1.186 V, but in practice this is not achieved. There are several reasons for this reduced voltage:

[a] The reversible methanol oxidation potential is not observed due to the occurrence of additional reactions involving formaldehyde and formic acid species, and a mixed potential results.

[b] The overpotential required to achieve useful currents is very high due to poisoning of the catalyst.

[c] The oxygen reduction electrode also has a mixed reversible potential due to peroxide formation, and suffers from a high overpotential, although not as severe as the methanol electrode.

The main problem still to be overcome with the DMFC is primarily electrocatalytic and is associated with the need to reduce substantially the overpotential at the anode. To explain the nature of the problem it is necessary to look at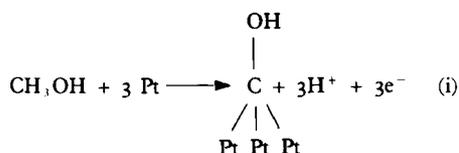 the generally accepted reaction mechanism for the oxidation of methanol on a platinum electrode. This is reviewed in detail in the literature (7, 19), but a brief outline is given here.

Several views have emerged over the past decade concerning the details of the electrooxidation mechanism. One of the most widely accepted theories has been put forward by Breiter (20). He proposed a "parallel paths" reaction scheme, one path going by way of formaldehyde and formic acid to carbon dioxide, and the other by adsorption and dehydrogenation of the methanol molecule on the platinum catalyst followed by further oxidation of the tenaciously held dehydrogenated organic fragment to carbon dioxide:

$$COH \longrightarrow CO_2$$
$$CH_3OH \longrightarrow$$
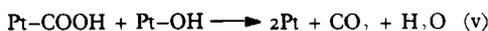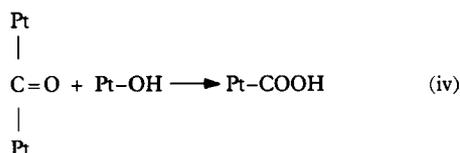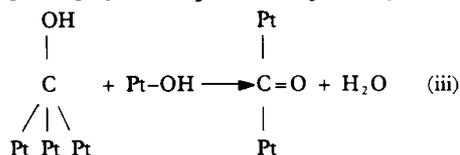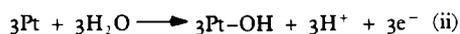$$CH_2O \longrightarrow HCOOH \longrightarrow CO_2$$
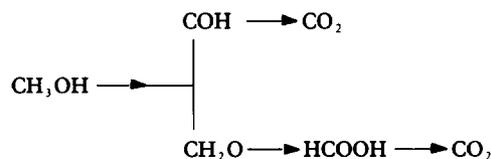
Traces of formaldehyde and formic acid have indeed been identified in solution, but it is the simultaneous build up of the dehydrogenated – COH residue that is thought to be responsible for the rapid diminution of the current. Much work has been carried out to investigate the nature of the adsorbed poison (7, 19) and

most evidence points to the reaction occurring by a stepwise removal of the hydrogens from the methanol molecule to leave a fragment of composition $-COH$ strongly chemisorbed to the platinum, as follows:

$$CH_3OH + 3\,Pt \longrightarrow \overset{\displaystyle OH}{\underset{\displaystyle /\,|\,\backslash}{\underset{\displaystyle Pt\ Pt\ Pt}{C}}} + 3H^+ + 3e^- \qquad (i)$$

However, recent workers have used in-situ spectroscopic studies to show that the adsorbed species is likely to be CO single bonded to a platinum atom (21, 22). The next stage involves the reaction of the "poison" with adsorbed H_2O or OH to form CO_2. High potentials are required for the adsorption of such oxygen-containing species and thus this reaction only proceeds at potentials substantially anodic to the methanol reversible potential. There is again some argument as to the nature of this oxygen-containing species since catalyst activity is observed at potentials lower than that at which the electrosorption of water to produce adsorbed OH species is expected. Wieckowski has suggested that the oxidation proceeds via an adsorbed (possibly strained and therefore reactive) water molecule (23). However, the generally accepted scheme involves the reaction of the $-COH$ species with OH species adsorbed on platinum as follows:

$$3Pt + 3H_2O \longrightarrow 3Pt\text{-}OH + 3H^+ + 3e^- \quad (ii)$$

$$\overset{\displaystyle OH}{\underset{\displaystyle /\,|\,\backslash}{\underset{\displaystyle Pt\ Pt\ Pt}{C}}} + Pt\text{-}OH \longrightarrow \underset{\displaystyle Pt}{C=O} + H_2O \qquad (iii)$$

$$\underset{\displaystyle Pt}{\overset{\displaystyle Pt}{\underset{\displaystyle |}{|}}}$$

$$\underset{\displaystyle Pt}{C=O} + Pt\text{-}OH \longrightarrow Pt\text{-}COOH \qquad (iv)$$

$$Pt\text{-}COOH + Pt\text{-}OH \longrightarrow 2Pt + CO_2 + H_2O \quad (v)$$

This mechanism assumes that the catalyst must be dual functional, that is to say it must electrosorb methanol and water in the same potential region. Several workers have measured initial currents which were 10,000 to 100,000 times higher than the so-called steady state current which was found after a few minutes on an anode test (24). The reason for the rapid deactivation is thought to be build-up of the $-COH$ residue on the catalyst surface, since, while platinum effectively adsorbs methanol at low potentials, it does not perform so well in the adsorption of water, and for this reason is not a particularly effective catalyst.

The activity of a methanol oxidation electrode depends on several factors including catalyst formulation, the catalyst support, the electrode structure and the operating conditions selected. Most work has concentrated on examining the effect of changing the catalyst formulation. Platinum group metal-containing catalysts are the only systems to date to show any activity for methanol oxidation at low potentials. Many workers have made bimetallic and trimetallic catalysts with platinum in the hope that poisoning by the methanolic residue would be significantly reduced or eliminated. Most of the d block elements have been tried as well as germanium, tin, lead, arsenic, antimony, bismuth, sulphur, selenium, tellurium and lithium. Various theories have been put forward to explain the promoting effect of the additional elements and this area remains controversial (25, 26). The best element combinations reported are platinum/ruthenium, platinum/tin, platinum/rhenium, platinum/titanium, platinum/osmium, platinum/ruthenium/tin and platinum/ruthenium/gold. Although it is not certain by which method these elements enhance activity, increases of up to 40 times have been recorded. Platinum/ruthenium is often reported to be the most active combination, and Shell, Esso and more recently, Hitachi, have favoured this system.

A European Research Programme

The Commission of the European Communities (CEC) has recently initiated work on direct methanol fuel cells as part of the "Non Nuclear Energy Research and Development Programme". The direct methanol fuel cell

Fig. 3 In the methanol electro-oxidation process the activity of a platinum catalyst can be enhanced by the addition of metal promoters. Ruthenium has the greatest effect and is currently the favoured promoter

Half cell conditions:
   Sulphuric acid 3M
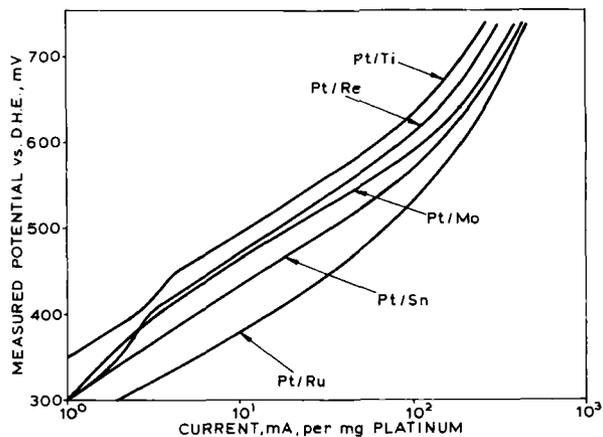   Methanol 1M
   Temperature 60°C

Fig. 4 The performance of the methanol oxidation electrode can be influenced by changing the electrolyte. In alkaline solution, that is at high pH, the reaction is enhanced significantly but alkaline electrolytes suffer the disadvantage of carbonation which ultimately causes de-activation
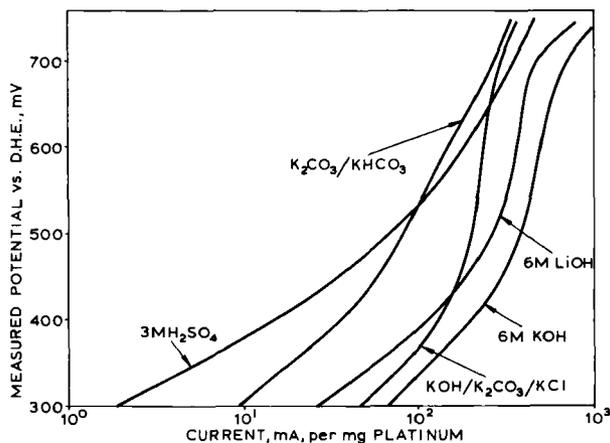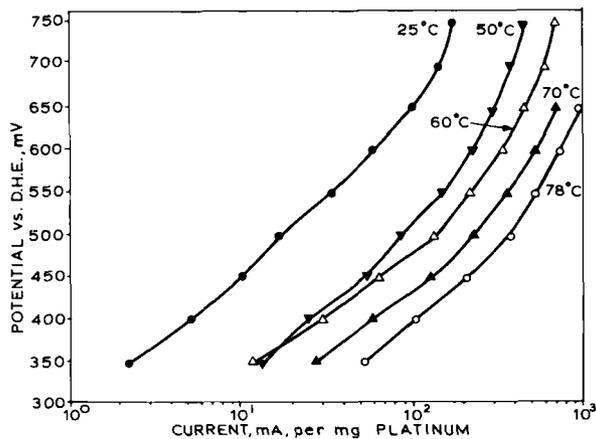

Fig. 5 The performance of the direct methanol fuel cell may be enhanced by increasing the stack operating temperature, although the temperature increase must be limited to prevent methanol loss by vaporisation

Commission of the European Communities Fuel Cell Programme	
Participant	Subject of Study
Johnson Matthey Technology Centre (U.K.)	Noble/base metal catalysts for methanol oxidation, half cell and full cell studies
University of Oxford (U.K.)	Fundamental studies of the anode reaction on noble metal and base oxide materials in collaboration with Johnson Matthey Technology Centre
University of Southampton (U.K.)	Ultra high vacuum studies of electrochemical behaviour of methanol oxidation on platinum single crystals
C.N.R.S. (France)	Electrochemical characterisation of methanol oxidation on platinum single crystal surfaces
Université de Poitiers (France)	Liquid chromatographic and infrared reflectance spectroscopic studies of methanol electro-oxidation on polycrystalline platinum surfaces
Universität Bonn (Germany)	Investigation of co-catalysts for methanol electro-oxidation on platinum
Siemens A.G. (Germany)	Investigation of catalytic materials for methanol electro-oxidation — in collaboration with Bonn University
University of Cork (Eire)	Development of low-level noble metal cathodes for the reduction of oxygen

programme is due for completion in the Autumn of 1989 and has the following targets for performance: power density $50mW/cm^2$, noble metal loading $<1mg/cm^2$, temperature $<65°C$. The participants in the DMFC section are given above in the Table.
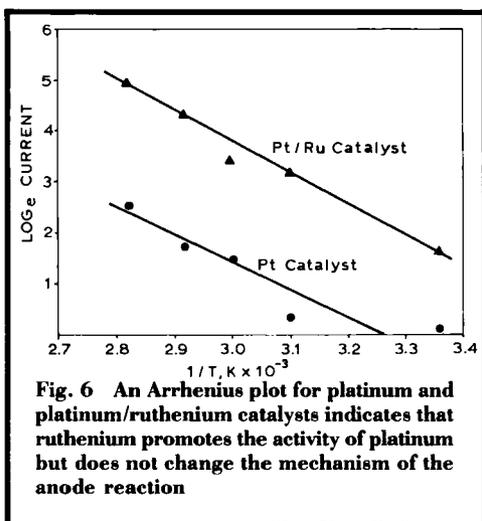
Recent Developments

Previous research has shown that under the operating conditions commonly employed (1M methanol, 3M sulphuric acid, 60°C) the activity of a pure platinum catalyst for methanol electro-oxidation can be enhanced by the addition of metal promotors, with ruthenium showing by far the greatest effect. Figure 3 compares the activity of a number of Johnson Matthey catalysts utilising platinum and a small percentage of a second metal component, dispersed on carbon. The current-potential curves (and all subsequent data) are shown uncorrected for solution resistance which was typically <0.2 ohms for the cell employed.

The platinum/ruthenium system has been studied in detail at the Johnson Matthey Technology Centre and an optimum catalyst formulation has been identified. Electrochemical half cell measurements have indicated that the activity of pure platinum can be increased from 5–6 mA/mg Pt at 400mV versus dynamic hydrogen electrode (D.H.E.) to 40–45 mA/mg Pt with the optimum platinum/ruthenium formulation. Due to economic constraints a compromise loading of 10% platinum on the catalyst has thus been identified. Subsequent data shown in the Figures refer to this catalyst unless specified otherwise.

The variation in performance for the anode reaction as a function of electrolyte is shown in Figure 4. From these results it is not possible to attribute the more favourable electrode kinetics directly to an increase in pH since the electrolyte composition changes. With porous electrodes, changes in electrolyte composition may result in subtle effects such as an alteration in the surface tension or the conductivity,

Fig. 6 An Arrhenius plot for platinum and platinum/ruthenium catalysts indicates that ruthenium promotes the activity of platinum but does not change the mechanism of the anode reaction

In addition, the activity of the oxidation catalyst has been found to be very dependent on operating conditions; the effect of increasing temperature on catalytic activity being shown in Figure 5. It is evident that, at temperatures as low as 80°C, activities in excess of 100 mA/mg Pt can be obtained. Figure 6 shows the Arrhenius plots for platinum and platinum/ruthenium catalysts with apparent activation energies of 36 kJ/mol and 49 kJ/mol, respectively, although the margin of error makes precise interpretation difficult. These results suggest that ruthenium promotes the activity of platinum but does not change the mechanism of the anode reaction. At temperatures above the boiling point of methanol (65°C) loss of fuel due to evaporation must be considered, while operation at higher pressures (>1 atm) would necessitate separation of methanol from the carbon dioxide and water vapour exhaust gases.
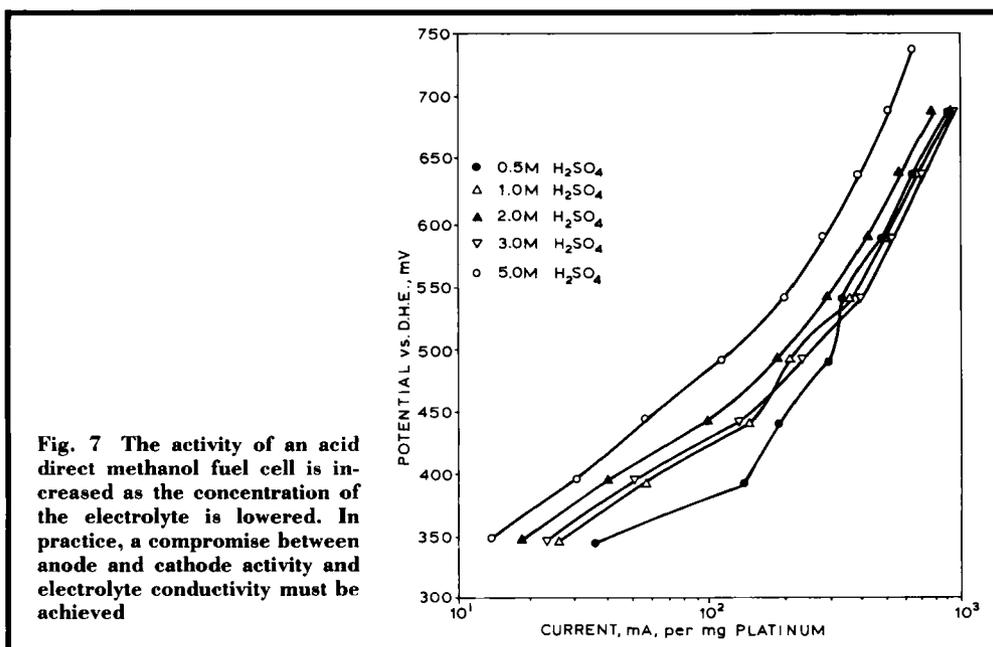
which may not be apparent on planar electrode surfaces.

Thus the interpretation of Figure 4 requires some caution. However, from thermodynamic considerations the open-circuit potentials of the anode and cathode reaction are predicted to shift to more negative values as the pH of the electrolyte increases.

The effect of sulphuric acid concentration on activity is shown in Figure 7, where it can be seen that activity increases as the acid concentration is decreased. This can be rationalised most easily in terms of competition between the electrolyte ions and methanol/water for catalyst

Fig. 7 The activity of an acid direct methanol fuel cell is increased as the concentration of the electrolyte is lowered. In practice, a compromise between anode and cathode activity and electrolyte conductivity must be achieved

sites. A decrease in acid strength appears desirable in terms of catalyst activity and also in terms of electrode stability since many potentially useful catalyst materials dissolve in highly acidic media. However the conductivity of the system must be kept as high as possible in order to avoid resistive losses and this will place considerable constrains on the choice of electrolyte.

The performance of a variety of fuels during electro-oxidation in 3M sulphuric acid on a platinum/ruthenium catalyst is illustrated in Figure 8. The best activities are obtained with formic acid despite the fact that this molecule only liberates 2 electrons during oxidation compared with methanol which liberates 6 electrons. Unfortunately the aggressive chemical nature of formic acid precludes its use in commercial systems.

Conclusions

The development of advanced anodes for the direct methanol fuel cell has been limited not only by the complexity of the electrode reactions but also by the difficulties inherent in studying porous electrodes. Clearly, any attempt to improve the performance of a real,

that is to say a porous electrode must take the structure of the electrode into account. In this respect the improvements obtained with bi-metallic catalysts need careful interpretation as the addition of a second metal in the catalyst dispersion may change both the physical as well as the chemical nature of the active site (26). However, further refinement of the platinum/ ruthenium bimetallic catalyst prepared on traditional carbon dispersions is unlikely to yield an order of magnitude improvement in anode activity.

What is needed is a far greater understanding of the chemistry of the overall catalytic process coupled with a knowledge of how to reproduce the desired "molecular scale" properties in a practical electrode.

The majority of research has centred around the identification of the precise nature of the poisoning species formed on platinum. This is obviously a very important aspect and recent developments in the use of spectroscopic techniques to probe the electrochemical interface in-situ promise to finally resolve the issue. In addition, there are a number of other aspects of the electro-oxidation reaction that require
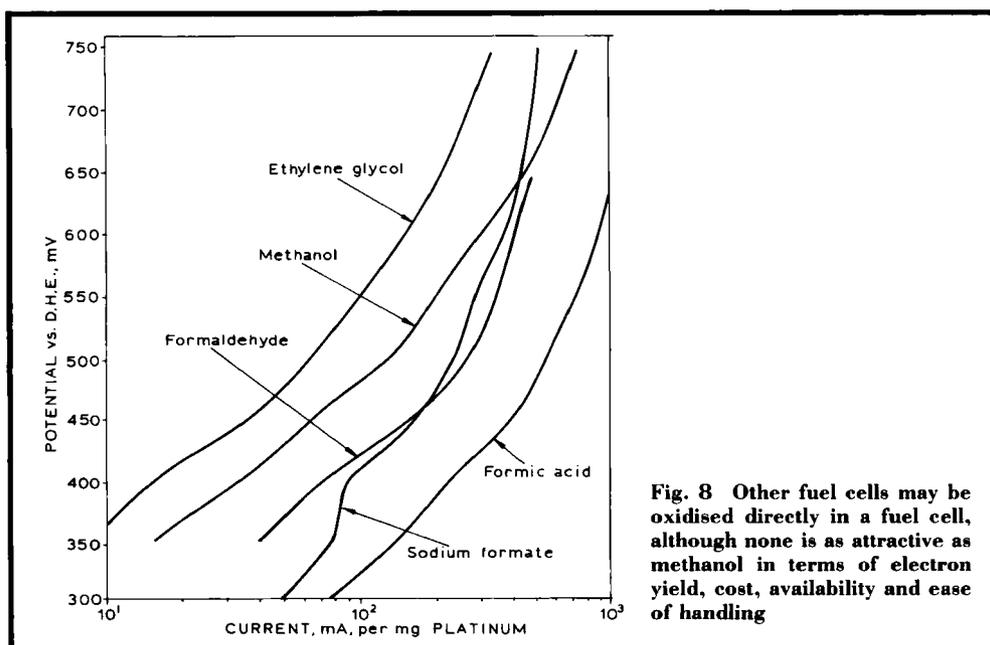

Fig. 8 Other fuel cells may be oxidised directly in a fuel cell, although none is as attractive as methanol in terms of electron yield, cost, availability and ease of handling

attention as a matter of urgency. These are:

The function of co-catalysts (such as bimetallic catalysts)

Exploration of alternative electrolytes

Optimisation of porous electrode structure.

In conclusion, it is hoped that the broad approach taken by the participants of the CEC Research Programme in tackling the problems outlined above will lead to the development of more cost-effective direct methanol fuel cells.

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Fabricating Platinum Disc Microelectrodes

A variety of electrochemical studies depend upon the use of microelectrodes, and if an electrode disc of sub-micron proportions is used ohmic distortion is virtually eliminated. Disc microelectrodes have been produced by encapsulating a fine Wollaston wire in glass and also by vapour deposition, but an easier method has now been reported by K. Itaya, T. Abe and I. Uchida of Tohoku University, Japan (*J. Electrochem. Soc.*, 1987, 134, (5), 1191–1193).

Anodic electropolishing is used widely to prepare sharp points on needle-like metal specimens that are to be examined by field ion microscopy, and this technique has been adapted to produce microelectrodes. The smoothest surface was obtained using a molten salt of sodium nitrate and sodium chloride (4 to 1, by weight) held at a temperature of 320±10°C; this being contained in a platinum crucible which served as a counter electrode while a platinum wire with a diameter of 65μm was dipped in the melt and anodically polarised by a periodic square wave, the amplitude of which affected both the shape of the pointed tip and the smoothness of the surface.

Tapered platinum wires with radii 100nm have been produced relatively easily; such tips are then encapsulated in epoxy resin, or a similar sealing material, and the electrode surface exposed by cutting through the composite with a diamond knife attached to an ultramicrotome. It is suggested that this method could be extended to iridium and gold, and even to carbon, using an alkali solution.