Direct methanol–air fuel cells for road transportation

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Abstract

The direct methanol–air fuel cell is reviewed with special attention to its use in road transportation applications. The history of the technology is discussed and the various problems associated with its commercial development are assessed, in particular the mechanisms of the electrode reactions, the development of effective catalysts, and the possible electrolytes which can be used. The barriers to successful commercialization are reviewed and suggestions for future work are given. © 1999 Elsevier Science S.A. All rights reserved.

1. Introduction

In many respects, the direct methanol–air fuel cell is a promising electrochemical power source for electric vehicles (EVs). The device uses a liquid fuel which can be derived from oil, natural gas, coal, or biomass. Thus, there are no limitations on the availability of methanol fuel. As a liquid fuel under normal conditions, methanol can be dispensed via the existing distribution and retail network in the transportation sector with, perhaps, only a few minor modifications. The power source does not require a mini-refinery under the hood of the vehicle to convert the fuel to hydrogen. The device and its auxiliary utilities are therefore of a convenient size for fitting into the engine compartment of even small private cars. Although no demonstration vehicles based on this power source have been built and operated, it can be concluded that with operation at 60 to 80°C, the emissions from such vehicles (especially nitrogen oxides from the air feed) would be considerably lower than those of conventional internal-combustion-engined vehicles (ICEVs). Principally, carbon dioxide and water would be emitted, but the possibility of some formaldehyde cannot be excluded. Because of the inherent greater efficiency of fuel cells, the production of carbon dioxide would be at a substantially lower level than

that from ICEVs. In city driving, this advantage would be even greater. This is because the efficiency of a fuel cell increases as the load on the cell decreases, i.e., behaviour which is the reverse of that experienced with heat engines.

Why, therefore, do we not see vehicles powered by direct methanol–air fuel cells on our streets today? The answer is quite simple. The performance of the state-of-the-art cell at an acceptable cost is substantially poorer than that required for road transportation applications. Additionally, we should not underestimate the technological advances which have been made over the last century, and particularly during the last 20 years, in the performance of the competition, namely, internal-combustion and external-combustion engines. Such engines in modern vehicles cost only a few tens of dollars per kilowatt, and this provides very severe competition indeed.

Almost certainly, the direct methanol–fuel cell will require platinum-based catalysts for the fuel electrode, and probably also for the air electrode. Given the high cost of platinum, the amount of the metal must be minimized in order to match the cost of an equivalent heat engine. In addition, there is the question of the availability of platinum supplies. It has been estimated [1] that if 50 million vehicles powered by such a device were manufactured each year, then the amount of platinum required would far exceed the current production of platinum. Although more than 95% of the platinum would be recoverable at the end of a vehicle's life, the issue of platinum supply alone would still present some difficulties. Nevertheless, if the

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catalytic problem can be solved and sufficiently small amounts of platinum can prove effective, then a substantial share of the vehicle market could be captured with all the associated benefits to the environment. Thus, the methanol–air fuel cell has been regarded by many as the 'philosopher's stone' for road vehicles—its successful development would greatly assist progress towards a sustainable transportation sector.

2. History of the direct methanol–air fuel cell

The history of the direct methanol–air fuel cell is neither as long nor as spectacular as that of the hydrogen–air fuel cell which was first demonstrated by William Grove in 1839 [2] and, in modern times, by the late Francis (Tom) Bacon [3]. Bacon's work culminated in the use of hydrogen–air fuel cells in the Apollo Space programme and resulted in a diversification into alkaline, phosphoric acid, molten carbonate, solid oxide and solid polymer electrolyte technologies that have attracted considerable investment during the last 20 years. The direct methanol–air cell was pioneered by Shell Research in England and Exxon-Alsthom in France during the 1960s and 1970s. Shell took the acid electrolyte approach and used sulfuric acid, while Exxon-Alsthom adopted the alkaline electrolyte route after initial experiments with sulfuric acid.

Shell's interest in fuel cells began in the late 1950s; the aim was to discover whether the fuel cell could be a competitive prime mover for road transportation. The Shell team took the view that operation close to ambient pressure and temperature was highly desirable. Air was seen as the only acceptable oxidant. At that time, all existing fuel-cell gas electrodes (e.g., Bacon biporous, Justi DSK and Kordesch carbon) were relatively thick and gave poor performance when operating on air and the reasons for this were thus sought. Having identified that the limiting factors were physical rather than chemical, it was reasoned that diffusion of oxygen into the electrolyte and of nitrogen away from the catalyst pores were the significant factors. The solution adopted by Shell was to create a very thin electrode with finely spaced pores by evaporating silver or gold on to a substrate of very uniform, microporous, polyvinyl chloride (PVC), which was in large-scale manufacture as separator material for lead–acid batteries. A layer of catalyst was then attached to the metallic layer. These composites functioned well on air and put Shell in a position to make fuel-cell electrodes of large area quite cheaply [4]. Initially, these electrodes were used in alkaline electrolyte. In order to give credibility to the idea that a fuel cell operating at ambient pressure and temperature could be a viable power source, a number of stacks were built and culminated in the construction of a 5-kW net unit. The pure hydrogen was generated from a methanol–water mixture and purified by a palladium–silver diffuser.

The whole unit was self-contained. The system took 15 min to start and thereafter offered instantaneous response to changes in load. Starting from below 0°C was also demonstrated [5].

It was recognized, however, that the above design was too complex and that direct oxidation of methanol was much to be preferred. As a methanol electrode in sulfuric acid, platinum itself was found to be rapidly poisoned by reaction products and this resulted in a wide range of platinum alloys being examined for catalytic activity [6]. This research by Shell found only platinum–ruthenium and platinum–rhodium to be effective; the former was favoured. At that time, Johnson Matthey had already provided Shell with Adams platinum (a bulk, but finely divided, platinum catalyst) which proved to be an outstanding catalyst for oxygen reduction in fuel cells and which, unlike platinum black, appeared to be immune to sintering. Platinum–ruthenium was subsequently provided and electrodes with 10 mg cm^{-2} gave results which encouraged the construction of stacks [4] in 1963. The simplicity of operation was attractive, not only was the exhaust carbon dioxide automatically separated by the phase change in the electrolyte, but the fuel electrodes (anodes) retained their correct negative potential during shutdown. This ensured that all the cells were of the correct polarity on start-up and cell reversal, which can occur in hydrogen–oxygen fuel cells, was not a problem. A 300-W unit, which powered its own auxiliaries, was built. Although the system proved to be reliable, the costs were excessive for all but very specialized purposes. Thereafter, Shell's efforts were devoted to reducing costs by greatly improving the catalysts.

Substantial progress was made by teams at the Shell Thornton Research Centre in Chester, UK, and at the Koninklijke Shell Laboratorium in Amsterdam, the Netherlands. During the period 1973–1981, the performance of the fuel electrode was improved by over two orders of magnitude and a more detailed understanding of the mechanism of the methanol oxidation reaction was obtained. At the same time, the Amsterdam laboratory made considerable progress in the development of stable, active, non-noble metal catalysts for the air electrode. Some of this work will be addressed later.

The engineering approach taken by the Exxon-Alsthom group in France with alkaline and buffer electrolyte technology was also impressive, but appeared not to offer much chance of commercial exploitation since Exxon pulled out of the enterprise in the late 1970s.

In the early 1980s, as a result of the lower growth in oil consumption that resulted from the conservation measures taken after the 1973 crisis, it became clear that the fears of an imminent oil shortage were unfounded [7]. The consequent drop in oil prices pushed the target cost for the methanol–air fuel cell even further out of reach. Shell accordingly decided to cease all work on the device in 1981; the research team was disbanded and the members assigned to other areas.

During the 1960s, notable research was undertaken on the fundamental methanol electro-oxidation reaction by Vielstich [8], Breiter [9–12], Bagotsky and Vassilyev [13,14], Biegler and Koch [15], and others, and what understanding there is of the mechanism of the reaction owes much to these workers. More recently, spectroscopic techniques have been applied to study the reaction. The evidence from such investigations is conflicting and depends on the techniques used and the types of platinum catalyst studied. Thus, although the work has been of high quality, the true nature of the mechanism(s) has still to be determined.

In the mid-to-late 1980s, protection of the environment again came to the fore as a serious global issue. The source of this concern was not the private citizen but Governments. The first action arose in the USA through an initiative by the California Air Resources Board to curb the smog problem in Los Angeles [7]. Legislation of increasing stringency was passed there and this inevitably spread to Europe, particularly Sweden. The European Community (now the European Union) also began to impose similar controls on vehicle emissions. This activity has resulted in renewed and serious efforts to develop fuel cells for road vehicles. At the same time, via various demonstration programmes of multi-kilowatt and even megawatt fuel cells for stationary applications, the public has become more aware of what the fuel cell can offer. Today, as spin-offs from stationary fuel-cell programmes in Europe, Japan and the USA, significant efforts are being made to apply such technology in vehicles. The pioneers are Ballard Power Systems and Daimler-Benz with their solid polymer electrolyte technology. The approach is predominantly to utilize indirect hydrocarbon-burning fuel cells with the associated necessity of incorporating a reformer, or some such processor, under the hood of the vehicle. Nevertheless, a programme has been set up in Europe to study the direct methanol–air fuel cell and a number of possibilities are being studied that include a high-temperature version with gaseous methanol fuel.

With car manufacturers such as Daimler-Benz, Ford, General Motors and Toyota actively involved in the development of vehicles powered by fuel cells, the participation of the owners of fuel infrastructures is also imperative. Over the last year or so, oil companies such as ARCO, Mobil, Exxon and Shell have become involved via alliances with car manufacturers.

As mentioned earlier, the basic problem with the methanol–air fuel cell is poor catalysis. There are a number of similarities between the electrochemical oxidation of methanol and gas-phase dehydrogenation reactions of hydrocarbons. Consequently, there exists, particularly in the oil industry, considerable catalysis expertise which, if directed towards improving the catalysis of methanol electro-oxidation, could result in success. It is our view that opportunities have been missed in exploiting this resource —perhaps because, to date, the driving force for the fuel cell has been transitory. Now, it is for real and the opportunities are there.

3. The noble metal issue

Mention was made earlier of the need for platinum, at least as a component of the methanol electro-oxidation catalyst and probably too as a component of the air electrode catalyst. In the latter case, however, the possibilities of non-noble catalysts are more promising. Quite apart from the need to have a catalyst which is passive in an electrolyte solution of concentrated acid, until recently only platinum-based catalysts have demonstrated any appreciable activity for the methanol electro-oxidation reaction. [1]

Appleby [1] has calculated that if all road vehicles in the Year 2010 were powered with the much better performing hydrogen–air fuel cells which use a solid polymeric acid electrolyte, then the requirement for platinum would still be about five times the total amount of the metal that has been mined to date. Of course, such vehicles would not require catalytic converters which also contain platinum, but the amounts of platinum in such converters are one-to-two orders of magnitude less than those in fuel cells. The challenge to the developers of direct methanol–air fuel cells is even greater, given the much poorer performance of this system. On the other hand, there are some advantages to be gained with fuel cells. First, the platinum is more than 95% recoverable at low cost. Thus, Stonehart [16] has argued that the actual cost of the platinum catalyst is only the interest on the money required to purchase the catalyst during its lifetime plus the costs of recovery of the platinum from the used catalyst. Second, as shall be seen later (Section 4.3), there is substantial scope for improving the performance of the methanol electrocatalyst. Third, the world vehicle population will not be replaced overnight; it will be an evolutionary process in which the appearance or non-appearance of a platinum alternative catalyst will dictate the extent to which fuel cells penetrate the vehicle market.

In summary, therefore, neither the limited supply of platinum nor even the cost problem is seen to be sufficiently serious to place an embargo on the future research and development of the direct methanol–air fuel cell.

4. The catalysis issue

The performance of the direct methanol–air fuel cell is so far from that required for successful commercialization

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[1] It is assumed that any methanol–air fuel cell applied commercially will utilize an acid electrolyte in the form of a concentrated liquid or a solid because of the ability of such an electrolyte to reject the carbon dioxide generated in the reaction.

that there are no recent examples of units of the size suitable for road transportation. There were complete working methanol–air systems in the early days of fuel-cell evolution, but while these systems demonstrated the feasibility of constructing such power sources, the catalysts were not adequate for the technology either to compete with alternative power sources or to meet the demands of the consumer. This section therefore reviews the reactions which occur in the fuel cell, together with the progress which has been made in catalysis and the prospects for future advances.

4.1. Electro-oxidation of methanol

In acid electrolyte, the overall reaction of methanol electro-oxidation is as follows:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad E_r = 0.04\ V \tag{1}$$
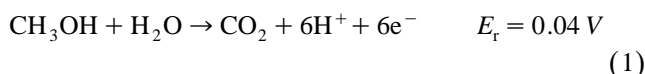
The methanol is adsorbed on to the platinum-based catalyst dissociatively with the release of hydrogen ions and, thus, the generation of large electric currents. Unfortunately, the dehydrogenation does not proceed to completion, otherwise there would not be a problem. A tenaciously held methanolic residue, the composition of which is still debated, remains and is slowly oxidized to carbon dioxide at higher potentials via reaction with water or other adsorbed oxygenated species. Such potentials are greatly higher than the reversible potential ($E_r = 0.04$ V) for methanol electro-oxidation, a major factor in the poor voltages of methanol–air fuel cells.
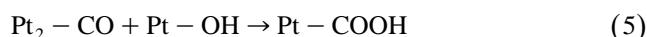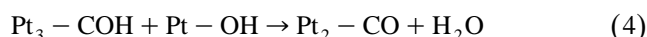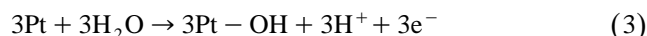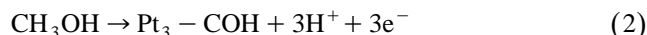
Electrochemical pulse techniques have been used [15,17] to study the electro-oxidation of methanol on smooth, platinum-foil catalysts in ultra-pure sulfuric acid. The initial currents decay by five orders of magnitude in going from the initial to a pseudo steady-state. The latter is defined as the current observed after 5 min on load. Even after this period, the current continues to decline and the true steady-state is only established after many hours. The origin of this massive fall in current is the coverage of the active platinum sites with the adsorbed methanolic residue which is only effectively removed at potentials where oxygen, in one form or another, is adsorbed. Thus, the challenge is to develop new catalysts which retard the formation of the dehydrogenated residue, without substantially lowering the activity, or which adsorb oxygen effectively at potentials much lower than that established on pure platinum.

The exact nature of the poisoning methanolic residue remains to be established despite considerable efforts to resolve its composition. In fact, there may be more than one type of residue. Compositions such as CO, COH, CHO and C_2O_3H have been suggested [9–14,18–29] on the basis of electrochemical, spectroscopic and radiotracer studies. Early evidence [18,19] pointed to the removal of the hydrogens from the methyl group to form the species $\underset{xxx}{C}OH$ (index xxx denotes three valence bonds with the surface), though later a formyl species ($\underset{x}{C}HO$) was proposed [22,23,29]. Complexes of similar composition (COH) have been found [30] in the liquid phase dehydrogenation of alcohols and other molecules on platinum catalysts. The reverse reaction, the electrochemical reduction of CO_2, has been reported [31] as leading to a complex of composition CHO, though whether this species is formyl or alcoholic in structure was not specified. It has been postulated [32] that a complex of composition COH is formed during the electro-oxidation of formic acid via reaction of the weakly held species $\underset{x}{C}OOH$ with adsorbed hydrogen. Studies of the influence of adsorbed species such as bismuth, cadmium, lead and thallium on the activity of platinum for formic acid electro-oxidation attributed [33] enhanced activities to the suppression of hydrogen adsorption and, thereby, to the formation of tenaciously held $\underset{xxx}{C}OH$. Positive influences of ad-atoms have also been found for methanol electro-oxidation, although here the mechanism of enhancement may be different since there is little or no evidence to suggest that $\underset{x}{C}OOH$ is formed during the initial dehydrogenation stage of the reaction, although it may be produced during a later stage.

The mechanism of the removal of the adsorbed species in methanol electro-oxidation is also not clear. The problem lies in the nature of the oxygen species that effects the removal of the residue. Some activity is observed at potentials well below that where electrosorption of water to produce adsorbed OH species is expected. This has led some workers [34] to suggest that adsorbed molecular H_2O may be responsible for the removal of the residue. On the other hand, only very small amounts of adsorbed OH may be necessary to initiate the reaction.

The most generally accepted mechanism for methanol electro-oxidation involves the reaction of the adsorbed species with adsorbed OH [26]. If the adsorbed species is assumed to be a $\underset{xxx}{C}OH$ species attached via the carbon atom to three platinum sites, then the following scheme can be written:

$$CH_3OH \rightarrow Pt_3 - COH + 3H^+ + 3e^- \tag{2}$$

$$3Pt + 3H_2O \rightarrow 3Pt - OH + 3H^+ + 3e^- \tag{3}$$

$$Pt_3 - COH + Pt - OH \rightarrow Pt_2 - CO + H_2O \tag{4}$$

$$Pt_2 - CO + Pt - OH \rightarrow Pt - COOH \tag{5}$$

$$Pt - COOH + Pt - OH \rightarrow CO_2 + H_2O \tag{6}$$

Note that, the adsorbed species $\underset{xxx}{C}OH$, $\underset{xx}{C}O$ and $\underset{x}{C}OOH$ are postulated in this mechanism and the rate-determining step is most probably the transformation of Pt_3-COH to Pt_2-CO. Infrared spectroscopic evidence has been found [27,35,36] for the existence of adsorbed $\underset{xx}{C}O$ species on smooth platinum during the methanol electro-oxidation

reaction with only small, weakly held concentrations of species containing oxygen and hydrogen. By contrast, mass spectroscopic studies on finely divided platinum have revealed [29] an adsorbent of composition C_xHO with the proposal that it is a formyl species attached to one platinum site.

Some evidence for the mechanism based on a $C_{xxx}OH$ poison was obtained from work at Shell [37,38] on finely divided platinum catalysts supported on carbon paper. Furthermore, during the operation of methanol–air stacks, ester-like smells were identified which were due to the presence of organic acids [39]. While radical dimerizations are frequently encountered in electrochemical processes, this type of reaction seemed unlikely since the acids were present in quantities which decreased only slowly on progressing up the homologous series. It was suggested that the acids are formed through attack of the methanol by HCOH radicals in which the carbon is bonded to two metal sites in a manner analogous to the Fischer–Tropsch synthesis.

The most highly dispersed platinum catalysts, prepared by activation in hydrogen, displayed poorer activity than catalysts of lower metal surface-area prepared by activation in air. If the best dispersed catalysts were sintered by heating at high temperature in air or by electrochemical cycling [38], the intrinsic catalytic activity increased and passed through a maximum (Fig. 1). This intriguing result stimulated investigations to examine the electro-oxidation of formic acid on the same catalysts. It was found that the catalytic activity increased in direct proportion to the surface area of the platinum metal (Fig. 2). The electro-oxidation of formic acid is considered to occur via the following mechanism:

$$Pt + HCOOH \rightarrow Pt - COOH + H^+ + e^- \qquad (7)$$

$$Pt - COOH \rightarrow CO_2 + H^+ + e^- \qquad (8)$$
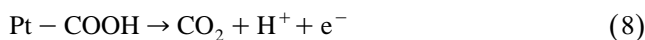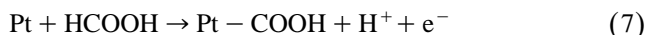
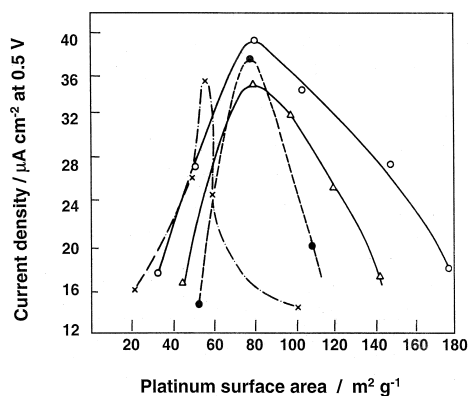Since the acid requires only one platinum site for electrosorption, increase in surface area of platinum increases

Fig. 2. Dependence of formic acid electro-oxidation on platinum surface-area: ($\times$, $\bigcirc$) catalyst sintered by electrochemical cycling, two different batches; ($\bullet$) catalyst sintered by heating in hydrogen [38].

the number of single platinum sites and, consequently, the catalytic activity. Cyclic voltammetric measurements on catalysts exposed to the electro-oxidation of formic acid show clearly greater amounts of the adsorbed, but easily removable, COOH species on the more highly dispersed catalysts (Fig. 3).

In the case of methanol, as the surface area of platinum increases fewer multi-sites are available for the three-site adsorption of $C_{xxx}OH$ and thus the activity decreases. The occurrence of a maximum in the relationship between catalytic activity and surface-area may reflect the possibility that the electrosorption of water is also a structure-sensitive reaction. In fact, the dependence of water adsorption on platinum dispersion may be in the opposite direction to that of methanol adsorption. The above phenomena, it should be noted, are also consistent with the strongly adsorbed poisoning species being CO, provided that it is bridge-bonded, i.e., requires more than one site for adsorption. Studies of the kinetics of the reaction would be helpful in resolving this issue.

Fig. 1. Dependence of catalytic activity for methanol electro-oxidation on platinum surface-area: ($\bigcirc$, $\triangle$) catalyst sintered by electrochemical cycling, two different batches; ($\bullet$) catalyst sintered by heating in hydrogen; ($\times$) catalyst sintered by heating in argon [38].
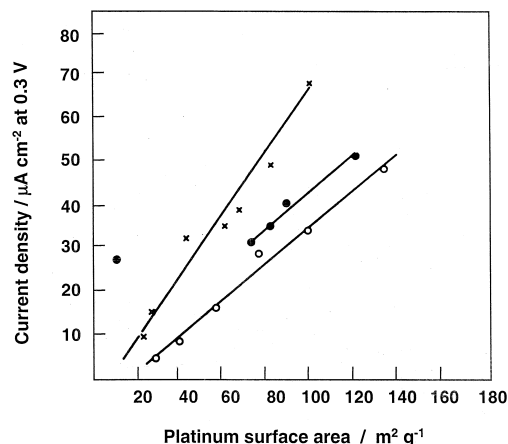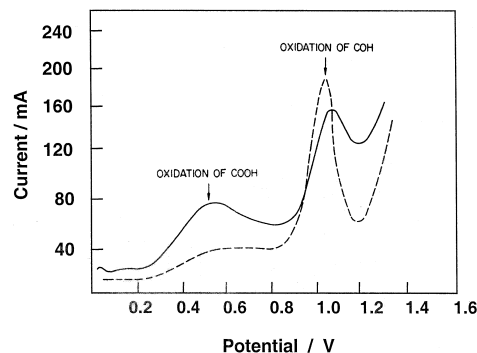

Fig. 3. Electro-oxidation of carbonaceous residues formed during formic acid electro-oxidation. Platinum area: (———) 136 m^2 g^{-1}, (– – –) 59 m^2 g^{-1}. 3 M H$_2$SO$_4$, 25°C, 50 mV s^{-1} [38].

It will, of course, not have escaped the reader's notice that the above observations are not exactly propitious since a natural aim in improving the performance of catalysts is to increase their surface area. The above observations imply that there is a point considerably above the level of atomic dispersion of platinum where enhanced surface area is not beneficial but, on the contrary, exacerbates the problem.

From the above, it is clear that to be effective for the methanol electro-oxidation reaction, a catalyst must be bifunctional—it must adsorb methanol and water (or other oxygen-containing species) in the same potential range and preferably close to the methanol reversible potential. Platinum and other noble metals, despite exhaustive searches for non-noble metal alternatives, remain the only catalysts to even approach these criteria, though recently some evidence has been found for activity with nickel-containing catalysts in acid electrolyte [40]. Unfortunately, platinum does not adsorb water very effectively at low potentials and even in a finely divided form, the activity in the steady-state does not approach that required for commercial application. There are, however, ways of modifying platinum to improve this situation, as shall become clear later.

The bulk of the above research, with the exception of the spectroscopic studies, was performed prior to 1980. Later reviews [27,41] of methanol electro-oxidation have discounted this earlier work, largely as a result of the spectroscopic studies which have identified CO as the adsorbed poison on smooth platinum. Such a conclusion is questionable, however, since the poison may be different on the finely divided types of platinum catalyst used in the pre-1980 investigations and recent studies using mass spectroscopy as opposed to infrared spectroscopy have revealed [16] that hydrogenated carbonaceous species such as COH are formed on finely divided platinum. Moreover, Hamnett et al. [42] have found no evidence for adsorbed CO on finely dispersed platinum catalysts using infrared techniques, and have proposed that the existence of oxidized species in some of the very small platinum crystallites influences the oxidation of methanol.

Thus, in concluding this discussion on catalysis, it can be said that despite all the work, both pre-1980 and thereafter, and the application of a plethora of electrochemical, spectroscopic and chemical techniques, the true mechanism of methanol electro-oxidation has still to be resolved. Certainly, it is not understood sufficiently to enable predictive development of commercially attractive catalysts.

4.2. The electrolyte

This section reviews the work which has been carried out on acid electrolytes for methanol electro-oxidation. Alkaline electrolytes are not discussed since, for reasons associated with their lack of invariance, they do not represent serious alternatives for fuel cells which use carbonaceous fuels.

Until fairly recently, the most intensively studied electrolyte was sulfuric acid, though there are a number of alternatives. Performance of the catalyst varies with the nature of the electrolyte and depends on factors such as the ionic conductivity, stability/invariance and corrosivity of the electrolyte, as well as the degree of adsorption of acid radicals on the surface of the catalyst. Thus, the performance of a particular catalyst for either the fuel or the air electrode can be affected quite dramatically by both type and composition of the electrolyte. The performance of a finely divided platinum catalyst for the electro-oxidation of methanol in sulfuric acid or phosphoric acid is shown in Fig. 4 [43]. The decrease in catalytic activity with increasing electrolyte concentration arises from the dual effects of lower water and higher electrolyte radical concentrations. It can also be seen that in the lower concentration region, sulfuric acid produces a better catalyst performance than phosphoric acid. This is due to the stronger acidity of sulfuric acid and the smaller poisoning effect of its acid radicals. At higher concentrations (> 5 M), the greater poisoning effect of the larger proportions of undissociated sulfuric acid results in a switchover to better performance in phosphoric acid. Nevertheless, 3 M H_2SO_4 has remained the optimum electrolyte for low-temperature ($<$ 60°C) methanol–air fuel cells. Little attention has been paid to operation above this temperature using phosphoric acid or even solid electrolyte. With the advancement of the technology of phosphoric acid fuel cells that has resulted from research programmes in the USA and Japan on high-temperature (200°C) units fuelled by reformed hydrocarbons and methanol, there may be opportunities for developing a high-temperature methanol–air system fuelled by gaseous methanol. Some work has been done in the USA [44] using 96% H_3PO_4 at temperatures of 205°C and results which are quite reasonable are presented in Fig. 5.
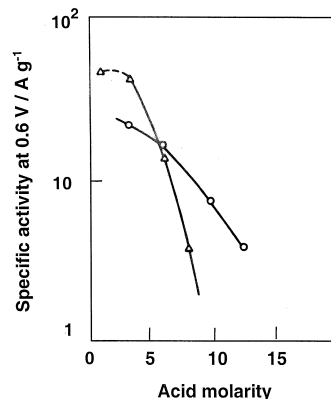

Fig. 4. Activity of electro-deposited platinum catalyst in ($\triangle$) H_2SO_4 and ($\bigcirc$) H_3PO_4 electrolyte. 1 M CH_3OH, 60°C [43].
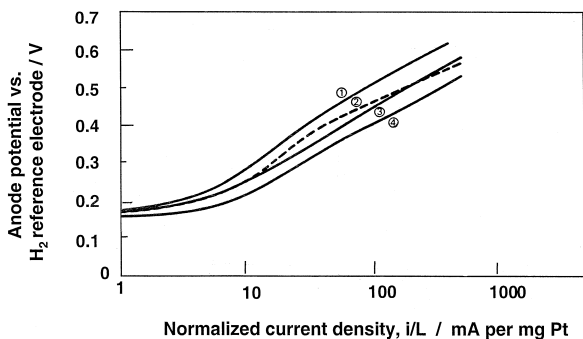
Fig. 5. Performance of various platinum-containing catalysts in 99.5% H_3PO_4 electrolyte at elevated temperature (205°C): (1) Pt–C, 0.5 mg Pt per cm^2; (2) Pt–Ti/C, 0.5 mg Pt per cm^2, ~ 0.05 mg Ti per cm^2; (3) Pt–Sn/C, 0.5 mg Pt per cm^2, ~ 0.05 mg Sn per cm^2; (4) Pt–Ru/C, 0.5 mg Pt per cm^2, 0.0775 mg Ru per cm^2 [44].

Fig. 7. Performance of platinum–ruthenium Adams catalyst in (– – –) 3 M H_2SO_4 at 60°C, and in 25% CF_3SO_3H at: (△) 25°C; (▲) 35°C; (□) 45°C; (○) 60°C. 1 M CH_3OH [47].

There has also been some interest in the use of trifluoromethane sulfonic acid (TFMSA) for application as an electrolyte in fuel cells [45]. It has been claimed that smooth platinum catalysts display higher activity for methanol electro-oxidation in the monohydrate of TFMSA than is exhibited in 0.5 M H_2SO_4 [46]. The activity for oxygen electro-reduction is also high in this medium. A comprehensive study of TFMSA monohydrate ($CF_3SO_3H \cdot H_2O$) and diluted TFMSA was carried out at the Shell Thornton Research Centre [47]. TFMSA monohydrate is a very strong acid, compared with perchloric acid, and as its acid radical is not strongly complexing it should, in principle, be an ideal electrolyte for fuel-cell reactions. The results of the investigation were disappointing: in the monohydrate, very low activities for the reaction were found with both smooth and finely-divided platinum catalysts (Fig. 6). Even in diluted versions in the range 10 to 50% TFMSA, the activities were only comparable with those found in 3 M H_2SO_4 (Fig. 7). Moreover, decomposition of the diluted electrolyte occurred above 80°C and produced a sulfur species which poisoned the catalyst and resulted in the total disappearance of the catalytic activity.
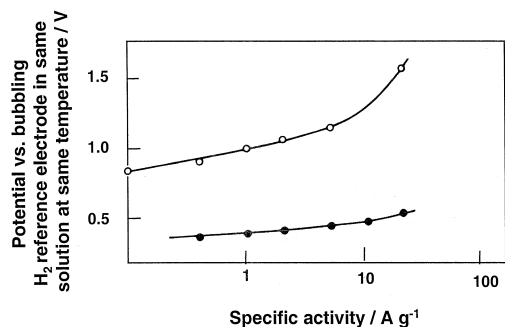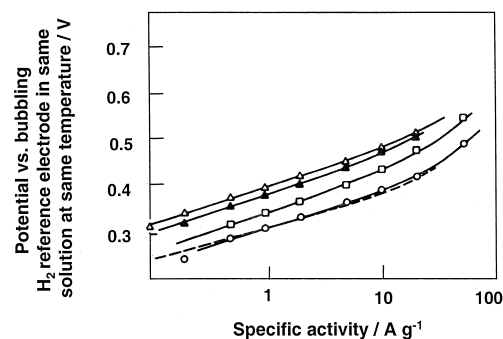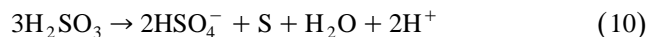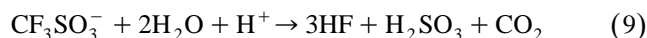

Fig. 6. Performance of platinum Adams catalyst in: (○) $CF_3SO_3H \cdot H_2O$; (●) 3 M H_2SO_4. 1 M CH_3OH, 80°C [47].

It has been speculated [48] that such behaviour is due to the following reactions:

$$CF_3SO_3^- + 2H_2O + H^+ \rightarrow 3HF + H_2SO_3 + CO_2 \qquad (9)$$

$$3H_2SO_3 \rightarrow 2HSO_4^- + S + H_2O + 2H^+ \qquad (10)$$

Under normal conditions, CF_3SO_{3-} is kinetically stable up to 550 K. It is possible, however, that in the presence of the platinum catalyst or through some effect of methanol, decomposition can occur at lower temperatures. Interestingly, this decomposition was not exhibited by the monohydrate, probably because of the much lower water activity.

Others workers [49] have disputed the Shell group's findings and have claimed that no decomposition could be found. Accordingly, the formation of sulfur species was ascribed to the presence of an SO_3 impurity in the TFMSA used by the Shell group. This does not seem a likely explanation since the same source of TFMSA was used in both studies. Thus, there has been no resolution of this issue. It would appear that no further work on the application of TFMSA in methanol–air fuel cells has been published.

Buffer electrolytes could conceivably be utilized as electrolyte, e.g., carbonate/bicarbonate. The problem here is that an equilibrium mixture of the buffer has to be maintained at the operating temperature of 60°C for the electrolyte to be invariant. When cooled to room temperature, however, one of the components precipitates out with adverse consequences for the operation of the air electrode. Apart from this, catalytic activities in such buffers are not significantly higher than in sulfuric acid.

Thus, as far as low-temperature (60°C) methanol–air fuel cells are concerned, there is no alternative at present to sulfuric acid, with the possible exception of solid polymeric acid electrolytes. Nakajima [50] has investigated methanol–air fuel cells which use these latter electrolytes and promising results have been obtained at 80°C, particularly when the platinum catalyst is modified by adsorption

of molybdenum species. This enhancement is only favourable in an operating region of low current density. At the Los Alamos Laboratories [51], interesting results have been obtained at temperatures above 100°C with power densities only some two-to-three times lower than those for reformate/air (indirect) fuel cells. Nevertheless, fuel efficiency is still low at only 50% due to the problem of methanol crossover. Workers at the Jet Propulsion Laboratory in collaboration with others [52] and also Küver and Vielstich [53] have claimed that the crossover problem can be reduced greatly by using newly developed polymer membranes. At higher temperatures, there are still other problems to be solved. For example, suitable methanol gas-diffusion electrodes need to be developed. Much can be learned, however, from the great amount of work done at high temperatures on phosphoric acid and solid polymer electrolytes in recent years.

4.3. Catalysts for methanol electro-oxidation

As mentioned earlier, there is no known non-noble metal catalyst identified for methanol electro-oxidation other than the recent work on nickel-based catalysts [40]. There have been claims made for certain metallic borides [54,55], but these have not been reproduced by other workers. Thus, we are almost certainly left with platinum-based catalysts and the need to maximize the activity. As discussed above, there is plenty of room for improvement, namely, five orders of magnitude increase in activity from pseudo steady-state to initial activity [15,17]. In relation to the aforementioned calculations by Appleby [1] regarding the limited availability of platinum for fuel-cell-powered vehicles, the pulse studies have shown that there is sufficient scope for improvement in the steady-state activity of platinum-based catalysts to address this problem. On the other hand, it is not just a question of activity but also of stability—after all, the activity has to be maintained. When run on continuous load, the 'steady-state' activity of present catalysts continues to decline over many thousands of hours, hence the use of the term 'pseudo steady-state'. It should be noted, however, that recent work at the Jet Propulsion Laboratory [52] has demonstrated good stability over 2000 h of operation with a solid polymer electrolyte.

An impressive body of knowledge has been built up over the years in the field of heterogeneous catalysis of gas-phase reactions, and particularly in the field of alloy catalysts. In these catalysts, the adsorption and catalytic properties of platinum are modified via the incorporation of a second, less expensive metal. Such technology has been applied to the field of electrocatalysis where various platinum-based binary catalysts have shown impressive increases in catalytic activity for methanol electro-oxidation. For example, several second components have been incorporated as adsorption stabilized sub-monolayers in the surface of finely divided platinum [56]. Substantial enhancements in activity were found for platinum modified with rhenium, ruthenium, tin or titanium. Other workers [57–60] have demonstrated large increases in activity for platinum modified with rhenium, ruthenium or tin prepared by more conventional methods. Originally, the function of a second component such as rhenium or tin was felt to be that of a redox co-catalyst with the methanol adsorbing and dehydrogenating on the platinum whilst the poisoning residue was chemically oxidized on the co-catalyst which itself was re-oxidized electrochemically. While this is an elegant theory, no evidence, such as oxidation or reduction peaks for tin or rhenium in cyclic voltammograms, has ever been found for the existence of such a redox process. Accordingly, the preferred explanation is that the second component acts as an agent which alters the adsorption properties of the platinum via a ligand effect and/or promotes the adsorption of oxygen species at lower potentials. Pulse studies have shown [61] that whereas the initial activity of platinum is not significantly affected by incorporation of the second metal, the activity in the pseudo steady-state is increased by two orders of magnitude. This improvement could arise by the second component, as mentioned above, either serving to modify the adsorption properties of platinum such that the adsorption of the residue is weakened, or by promoting the electrosorption of water at lower potentials and thus accelerating removal of the residue [62].

The surface composition of bimetallic alloy catalysts can play a critical role in determining catalytic activity, and this probably accounts for the wide differences in activity found for the same metal combinations in different laboratories. The preparation technique for the bimetallic catalyst can strongly influence its surface composition, and a variety of techniques have been used. For example, it has been shown [63] for both finely divided platinum–ruthenium Adams catalysts and platinum–ruthenium supported on carbon-fibre paper that heating the catalyst in hydrogen at temperatures between 200 and 500°C produces a substantial drop in catalytic activity (Fig. 8). Cyclic voltammetric studies have revealed that the surface of these catalysts is substantially enriched in platinum (Fig. 9). Heat treatment in the presence of hydrogen should enrich the surface of the catalyst with the component which has the higher heat of adsorption of hydrogen, in this case, platinum. The original activity can be recovered by treatment in air at similar temperatures.

As with gas-phase catalysis, considerable improvement in catalytic activity can be obtained by supporting the metal catalyst on a conducting support such as graphitized carbon. A number of techniques can be used in the preparation of the catalyst to ensure the maximum level of dispersion. As discussed earlier, however, this procedure is only of benefit up to a point for methanol electro-oxidation on monometallic platinum. Above a certain level of dispersion in pure-platinum catalysts, no further increase in activity is found—in fact significant decreases in activity occur. The effect of metal dispersion on the activity of
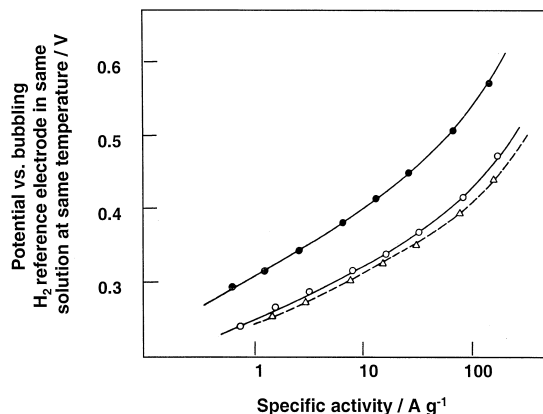
Fig. 8. Performance of platinum–ruthenium on carbon-fibre paper catalysts as a function of activation conditions: (●) activated in H_2 at 300°C, metal loading 0.69 mg; (○) activation in N_2 at 300°C, metal loading 0.73 mg; (△) activated in air at 300°C, metal loading 0.68 mg [63].

Fig. 10. Cyclic voltammograms for various finely divided platinum catalysts: (a) platinum Adams; (b) platinum on Cyanamid graphite; (c) platinum on untreated carbon-fibre paper; (d) platinum on electrochemically oxidized carbon paper. 3 M H_2SO_4, 25°C, 50 mV s^{-1} [65].

bimetallic catalysts has not been quantitatively studied and the best dispersion of bimetallics is still significantly below the maximum in the activity vs. dispersion curve for platinum. Until such studies are carried out, the situation with respect to activity vs. dispersion for bimetallic catalysts remains unclear.

The approach to improving catalyst dispersion is, first, to oxidize the carbon support either chemically or electrochemically to produce acidic surface oxides [64] which are then capable of complexing with metal cations via an ion-exchange process. For instance, in preparing platinum catalysts, the treated carbon (e.g., carbon-fibre paper) is ion-exchanged with $Pt(NH_3)_4(OH)_2$ in water, washed, dried at 120°C, and activated in air at 300°C [37,38]. This produces a catalyst with a surface area of up to almost atomic dispersion of the metal. Cyclic voltammograms for such a catalyst are shown in Fig. 10 and compared with those for conventionally prepared platinum catalysts [65]. Apart from displaying much better dispersions, the hydro-
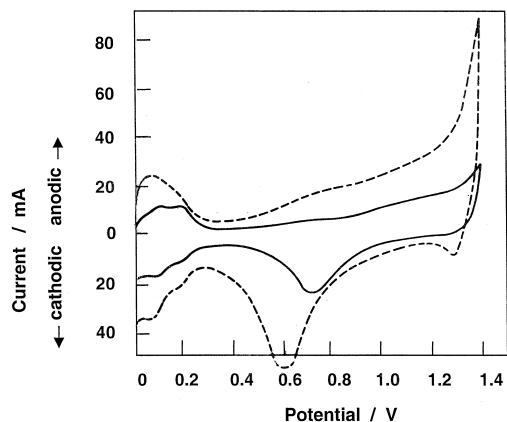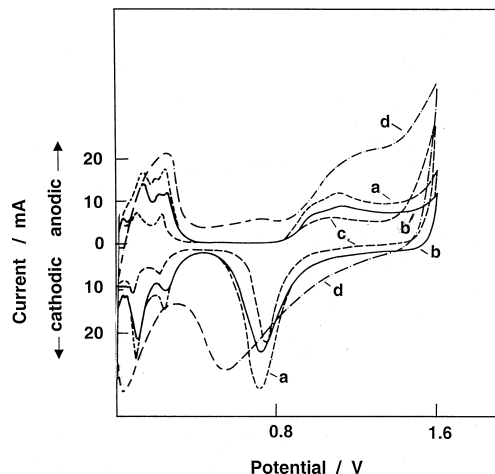
gen adsorption/desorption and oxygen adsorption and reduction regions are altered quite radically. This indicates that, in addition to the dispersive effect, the carbon appears to modify the surface of the platinum via a platinum–carbon interaction analogous to the modification of platinum produced by alloying with, for example, ruthenium or tin. Thus, the performance characteristics of such catalysts may be the result of a complicated effect between dispersion and surface modification. It should be noted that Hamnett et al. [42] have alluded to the peculiar oxidizing properties of very small platinum crystallites supported on carbon.

The preparation stages of the above catalysts have been characterized by means of differential thermal analysis (DTA) [37] and temperature programmed reduction (TPR) [66]. The studies showed that the properties of platinum are indeed modified by interaction with the carbon-paper support. DTA studies revealed that $Pt(NH_3)_4(OH)_2$ ion-exchanged on to oxidized carbon paper decomposes in air at much higher temperatures than bulk $Pt(NH_3)_4(OH)_2$, and thus confirmed that the $Pt(NH_3)_4^{2+}$ cation is coupled with the carbon surface. TPR on both dried and air-activated catalysts found that, after both stages of preparation, the reduction properties of the platinum species are different from those of catalysts prepared by simple impregnation of the carbon paper (Fig. 11). It is felt that the platinum–carbon interaction which causes the modification of the platinum properties is responsible, at least in part, for the enhancement of the catalytic activity. The situation is probably complicated, however, by the influence of the size of the platinum crystallites, as discussed earlier.

For bimetallic catalysts, particularly the platinum–ruthenium on carbon paper catalysts which were until recently the best catalysts for methanol electro-oxidation, ion-exchange type preparations remain to be developed. Thus far, only co-impregnation has proven to be success-

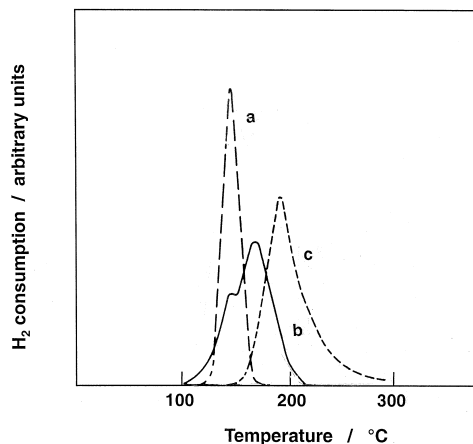Fig. 9. Cyclic voltammograms for platinum–ruthenium on carbon-fibre paper catalyst—influence of reduction in hydrogen. (– – –) Original catalyst activated in air at 300°C; (———) catalyst reduced in H_2 at 300°C. 3 M H_2SO_4, 60°C, 50 mV s^{-1} [63].

Fig. 11. Temperature-programmed reduction of platinum catalysts: (a) unsupported $Pt(NH_3)_4(OH)_2$; (b) impregnated supported $Pt(NH_3)_4(OH)_2$; (c) ion-exchanged supported $Pt(NH_3)_4^{2+}$ [66].

ful. This technique produces very effective catalysts (though the metal dispersion at typically 50 to 90 m^2 g^{-1} could be better), but only if certain conditions are applied during impregnation of the carbon. If aqueous solutions of H_2PtCl_6 and $RuCl_3$ are used, then very poor catalysts are produced. The most effective catalysts can only be obtained if complex salts such as $Pt(NH_3)_2(NO_2)_2$ and $Ru(NO)(NO_3)_x$ are used and are dissolved in the correct composition in concentrated nitric acid. The nitric acid solution appears to activate the carbon surface by oxidation, and the platinum and ruthenium species complex with the surface groups so formed. Studies using TPR and cyclic voltammetry have shown [67] that interaction with carbon occurs via ligand exchange between the nitrogen-containing groups of the metal complexes and nucleophilic surface groups formed on the carbon surface during oxidation by the nitric acid. The reduction of the resulting mixed-metal surface complex leads to the formation of the platinum–ruthenium catalyst which has greatly enhanced activity over that of pure platinum on carbon paper. Such binary catalysts have displayed an activity for direct methanol oxidation at 60°C of some 150 A per g platinum at a potential of 0.4 V on the hydrogen scale. This performance is difficult to compare with that obtained in the most recent studies [50,51] since the latter have been performed in different electrolytes and usually at higher temperatures. Nevertheless, it appears that the earlier performance is still respectable today.

To date, most work on catalyst development has concentrated on carbon-supported, platinum-based catalysts. There are obviously more effective supports for platinum, but the criterion that the support must be electrically conducting restricts the options. There remains substantial room for improvement in the dispersion of platinum and ruthenium, and the relationship between activity and dispersion must be established. No significant success has been achieved in effectively supporting platinum–tin or other interesting bimetallics on carbon—a situation which

is probably due to the lack of suitable complexing salts. Another approach may be to seek alternative procedures for modifying the carbon so that complexing with the salts used in the preparation of the catalyst proceeds more effectively. A very exciting recent development has been the application of 'combinatorial catalysis' (a technique used extensively in bio-organic systems) to the development of direct methanol electro-oxidation catalysts [68]. In this approach, a very large number of binary, ternary and quaternary noble-metal catalyst compositions in the form of an array of dots are prepared on a piece of conducting carbon paper. The dots are made by using a commonly available ink jet printer to deposit repeatedly inks of the individual metal components in different combinations. The catalytic activity of the array is screened in a special electrochemical cell which employs fluorescent acid–base indicators to detect activity on the basis of the lowering of the pH of the electrolyte as the reaction occurs. In this way, thousands of compositions can be rapidly screened and promising ones identified for conventional evaluation. A new, promising, ternary platinum–ruthenium–osmium catalyst has already been identified.

The long-term stability of catalysts for methanol electro-oxidation is poor. Even after the initial rapid decay of activity to the pseudo steady-state, the activity continues to steadily decline over thousands of hours. The effect is exhibited by both platinum and bimetallic catalysts. Although this would present a major problem for a methanol–air fuel cell continuously on load, in a transportation application, where a stop/start, full-load/part-load duty is encountered, the effect may not be so important. Shell Research and others have noticed that switching the current off for short periods of time results in a return of the catalytic activity to its pseudo steady-state level. This fortunate observation encouraged Shell to conduct life tests using various programmed on/off sequences; very little loss in activity was observed over thousands of hours [69]. In fact, a programmed sequence was developed to mimic the ECE 15 urban driving cycle of a vehicle and over 1000 h of steady operation was obtained. This property of self-recovery which the catalysts possess may even enable a methanol–air stack to deliver a high continuous power output, e.g., individual cells are switched off in rotation to recover whilst power continues to be delivered from the remainder of the stack—provided, of course, that such a procedure does not damage the performance of the air electrode. The Shell workers attributed the recovery to the simple removal of the carbonaceous residue at the open-circuit potential. Hamnett et al. [42] subsequently observed the same phenomenon but ascribed its cause, perhaps more reasonably, to the removal of inactive platinum oxide species at open-circuit.

4.4. Oxygen electro-reduction reaction

In this review, it is not proposed to examine extensively the substantial work conducted in the whole field of

oxygen electro-reduction, but rather to discuss the nature of the reaction and those catalysts which are considered as promising candidates for air electrodes in methanol–air fuel cells.

Given that the methanol–air fuel employs an acid electrolyte, the oxygen electro-reduction reaction is:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E_r = 1.229 \, V \qquad (11)$$

It has been proposed that the formation of water proceeds in a stepwise process via the formation of hydrogen peroxide [70], or by two parallel reactions [71], one which leads directly to water, the other to water via hydrogen peroxide. There is some evidence for the existence of the parallel-reaction mechanism in both acid and alkaline electrolytes.

In acid electrolyte, on which this discussion focuses, the reaction takes place at high, positive potentials. This results in a number of difficulties—at such potentials most metals dissolve and this gives rise to a similar situation to that prevailing at the fuel electrode, i.e., only noble metals and some of their alloys offer possibilities among metallic catalysts. Even when platinum is used, there are problems arising from the formation of surface oxides on the catalyst, which complicates the situation further despite the fact that oxides such as PtO_2 are good catalysts for the decomposition of hydrogen peroxide. This problem of metal dissolution and oxide formation could have even more drastic consequences during the long-term use of a fuel cell in transportation applications. In Section 4.3, it was shown how methanol catalysts are more stable when life-tested under the conditions which are likely to be encountered in road vehicles, i.e., varying current and stop/start service. The excursions to open-circuit during the time spent at zero current serve to regenerate the methanol electro-oxidation catalyst. Unfortunately, however, the time spent at open-circuit might cause some damage to the metal catalyst in the air electrode because of the high potentials involved, e.g., platinum crystallites may sinter and lose catalytic activity. This has certainly been shown (see, for example, Ref. [72]) to be a problem during the life-testing of platinum-containing catalysts for air electrodes in phosphoric acid fuel cells. Thus, operational difficulties associated with the air electrode reaction should not be underestimated.

4.5. Catalysts for oxygen electro-reduction

4.5.1. Noble metal catalysts

The most active catalysts for oxygen electro-reduction in acid electrolyte are platinum and certain platinum-containing alloys, though given that the fuel electrode must contain platinum, the amounts allowable for the air electrode would not produce the currents required for commercial success at the desired cell terminal voltage. Thus, work has concentrated on two areas, namely: (i) trying to improve the activity at the high positive potentials used;

(ii) attempting to develop non-noble metal complex catalysts—in particular macrocyclic organometallic chelates. The latter approach, if successful, would enable the whole of the allowable platinum inventory to be allocated to the fuel electrode and would thus ease the commercial target for that electrode and the consequent drain on world resources of platinum. Noble-metal catalysts are discussed here and alternative catalysts will be covered in Section 4.5.2.

The influence of platinum crystallite size has been examined by a number of workers [73,74]. Optimization of metal dispersion is required to maximize the utility of the metal inventory, and it is always a possibility that catalytic activity might be dependent on platinum crystallite size, as has been experienced with methanol electro-oxidation. Bett et al. [73] found no dependence of activity on crystallite size in the range 3 to 40 nm. Blurton et al. [74], however, investigated catalysts of much smaller crystallite size ($<$ 1.4 nm) and demonstrated that the activity decreased below this size. One possible reason for this behaviour may be a loss of metallic character by such small crystallites through metal–carbon interaction or from the dual-site requirement for dissociative oxygen adsorption. Ross [75], in studies of the reaction on single crystal faces, found that the reaction rate decreased in the order: $111 \gg 100 \gg 110$. It was considered that the varying platinum–platinum distances in the surface exerted an influence on the slow dissociation of adsorbed O_2H complexes. Stonehart [16], on the other hand, attributed the effects of crystallite size to an inter-particle diffusive interference between platinum crystallites. For example, when the distances between platinum crystallites of different size are the same, the specific activities are the same.

The main thrust of research in this area has been the attempt to prevent sintering of the platinum species during operation. On graphitized carbon, platinum can oxidize and recrystallize such that, over long periods of time, the activity falls and the metal itself may even be lost from the surface of the support. A further contributing factor is the oxidation of the graphite surface that can also occur under the conditions of the reaction. Various approaches have been taken to solve this problem, e.g., the use of other supports than carbon. For instance, it has been shown [76] that platinum sinters less readily when supported on semiconducting tin oxide and this was thought to be due to recrystallization of dissolved platinum on the low surface-energy tin–oxide support rather than on other platinum crystallites.

Some work has been done on depositing platinum on to carbon-coated γ-Al_2O_3, a procedure which leads to increased stability [77]. Other success in stabilizing platinum has been achieved [78] by alloying with a second metal component such as vanadium, and such catalysts have been used in high-temperature ($\sim 200°C$) phosphoric acid fuel cells [79]. Adzic et al. [80] have shown how adsorbed atoms can influence the activity of gold for oxygen reduc-

tion, and it is possible that further research in this area could lead to benefits in terms of both activity and stability. New electrolytes, e.g., fluorosulfonic acids, have been demonstrated as suitable electrolytes for oxygen electro-reduction [81] but, as discussed in Section 4.2, there may be problems with the fuel electrode in such a medium.

Considerable research has been conducted on alloys of platinum which range from binary alloys such as platinum–vanadium [78] and platinum–chromium [82], through to ternary alloys such as platinum–cobalt–gallium [83]. Enhancements in catalytic activity have been obtained via a variety of effects which have included the leaching of components (e.g., gallium) to produce porosity in the platinum and increasing the resistance of platinum to sintering [16].

The demands on a noble-metal air-electrode catalyst will be greater in a fuel cell used to drive an electric vehicle as opposed to one used to provide continuous power generation of power. This is, as mentioned above, the result of the stop/start duty of a vehicular fuel cell. It is ironic that such a duty enhances the performance of the fuel electrode catalyst.

4.5.2. Non-noble metal catalysts

Much research has been conducted on these catalysts in both acid and alkali electrolytes. In alkali, carbon has shown activity for the reaction, particularly when treated under certain conditions, e.g., heating in ammonia at high temperature, or adding small amounts of transition metals and activating in ammonia [84]. Surface groups, in particular basic surface oxides, are thought to play a role in the development of catalytic activity [85]. Various chalcogenide compounds, oxide spinels [86] and perovskites [87] have been claimed to display catalytic activity in alkali. Apart from carbon, however, none of these compounds is sufficiently stable in an acid electrolyte medium. Moreover, carbon exhibits little or no activity in acid.

Organometallic chelate catalysts hold the most promise for air electrodes in acid electrolyte [88]. Chelates such as phthalocyanines and porphyrins have structures (Fig. 12) similar to that of the enzyme catalase, which decomposes oxygen in living cells, and thus such materials have been examined for activity for oxygen electro-reduction. It has been suggested [89] that the planar structures of these macrocyclic compounds favour maximum interaction between oxygen and the central transition metal ion.

Since they are poor electrical conductors, the chelates are usually supported as thin layers on a conducting carbon substrate. It has been shown [90] that carbons with basic surface oxides are the most effective type of support. If supported on a metal such as gold, little activity is found [91]—it seems that interaction between the chelate and carbon is essential for the development of substantial catalytic activity. It has also been established [89] that the nature of the central metal ion in such chelates exerts a strong influence on activity. With phthalocyanines, for

(a) **Metal phthalocyanines**
     (MPC)

(b) **Metal tetra-azo-annulenes**
     (MTAA)

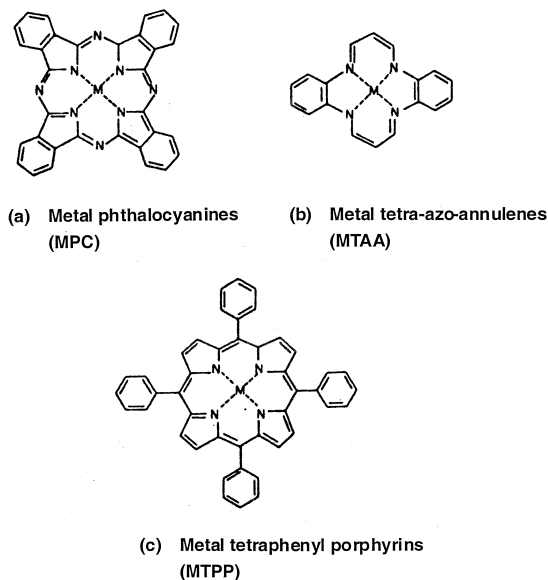(c) **Metal tetraphenyl porphyrins**
     (MTPP)

Fig. 12. Structure of some active chelates.

example, the most active catalysts are those where the central metal ion is iron or cobalt. It is also claimed [92] that the activity is affected by the substituents on the organic skeleton. Thus, the nature of support, the central metal ion, the type of chelate and the organic skeleton substituents may all influence the catalytic performance. Finally, the binding of the chelate to the carbon support via electron conduction bridges has been found to be beneficial [93].

Some workers have claimed [94] that the origin of the activity of carbon-supported chelates lies in the activity for H_2O_2 decomposition and that, intrinsically, the compounds do not catalyse the electro-reduction of oxygen. Other studies [95] have shown, however, that the chelates do indeed behave as oxygen-reduction catalysts, though they are also catalysts for H_2O_2 decomposition. The latter property is an essential feature of an air-electrode catalyst since should H_2O_2 be allowed to accumulate, it could have a detrimental effect on the stability and structure of the catalyst.

Various studies have been made to determine the mechanism of oxygen electro-reduction on such chelates. Beck [96] has proposed a redox mechanism based on the fact that chelates with a reversible metal redox couple in the region slightly below the reversible oxygen potential of 1.229 V usually demonstrate high activity. The central metal ion requires a redox potential such that it assumes its original valency after oxygen reduction. Correlations between redox potentials, gas phase activity, and reduction activity indicate, however, that the role of redox catalysis is not paramount [97–99].

It has been suggested that the bonding between oxygen and the central metal ion occurs via the d_z^2 orbital of the metal ion, and that back-bonding into the antibonding π^* orbitals of the oxygen molecule can take place via the d_{xz},

d_{yz} orbitals of the metal if they are occupied. In this way, the O–O bond is weakened. In order to activate the oxygen molecule, back-bonding is essential. The role of the support, the central metal ion, the substituents on organic skeleton and the different ligands on activity can be understood in this model. It may also be possible, via doping of the supported chelate catalyst with electropositive entities, to enhance this back-bonding effect in an analogous way to that by which N_2 dissociation is enhanced by the Haber ammonia synthesis catalyst, or CO dissociation is enhanced by the Fischer–Tropsch synthesis catalyst.

There have been several promising developments in the search for a practical, non-noble metal catalyst for the air electrode of an acid electrolyte methanol–air fuel cell. In particular, it has been discovered [100] that heat treatment of carbon-supported chelates can lead not only to substantial increases in activity but also to substantial improvements in long-term stability. For example, heating tetramethoxyphenylporphyrinato-cobalt-II between 800 and 1200°C produced a significant improvement in performance [101]. It was proposed that the carbon generated in the pyrolysis of the chelate was responsible for its enhanced electrochemical activity. In tests in 2.25 M H_2SO_4, a catalyst prepared by heat treatment at 800°C was stable for over 10 000 h at potentials ≥ 700 mV at a current density of 5 mA cm^{-2}.

A series of phthalocyanine complexes supported on Norit BRX carbon was examined by van Veen and Visser [95]. The results showed that the activity varied with the central metal ion as follows: Fe $\gg$ Co $\geq$ Ru $\geq$ Mn, Pd, Pt $\geq$ Zn. By contrast, the stability decreased in the order: Co $\geq$ Fe $\geq$ Ru. It was also established that carbon pretreatment to produce basic surface groups prior to emplacement of the chelate yielded the highest catalytic activity. After heat treatment at 700°C, the activity of the cobalt chelate increased by some 50-fold while stability also improved. On the other hand, the iron chelate did not display any improvement in activity, but did demonstrate much better stability. This and subsequent work has not completely clarified the process which takes place during the heat-treatment procedure, but it is possible that highly stable complexes containing a CoN_4 unit can be formed [102]. Certainly, at the temperatures involved, the organic skeleton of the chelate would be destroyed. Such complexes could conceivably be formed during the pyrolysis of transition metals containing carbon in the presence of ammonia [84].

Fabjan et al. [103] have obtained very impressive activities for oxygen reduction using catalysts prepared via pyrolysis of nitrogen-containing polymers such as polypyrrole on carbon-containing transition metal ions. This behaviour is presumably analogous to that reported above for the porphyrins. Both activity and stability were improved by the pyrolysis. Further studies of the influence of the chain length, the structure and the conductivity of such polymers are warranted.

As for the fuel electrode, little work has been done on the scale-up of chelate or other polymeric catalysts into practicable fuel-cell electrodes and it may be prudent to consolidate the work done so far by demonstrating that effective large-scale air electrodes can be made from such materials.

5. Non-catalytic aspects

There are several problems, other than catalysis, to be solved in the development of direct methanol–air fuel cells. The diffusion of the methanol fuel to the air electrode, for example, can cause the following difficulties. Chemical oxidation of the methanol can occur on the air electrode catalyst (particularly if it is platinum-containing) and thus lower the current efficiency of the fuel electrode. In addition, fuel can be lost by evaporation into the air stream, again leading to further losses. The chemical oxidation problem is not serious if chelate-type or polypyrrole catalysts are used in the air electrode. The evaporation of fuel can be reduced or eliminated by incorporating condensers in the exhaust stream of the air electrode. Similarly, maintenance of the water balance in the system sometimes has to be achieved by using condensers, otherwise the electrolyte changes concentration. Usually, the cell would be run at an operating temperature where evaporative losses of water are balanced by the amount of water formed during the reaction. Obviously, some of these problems become more severe if the operating temperature is raised above 60°C. Given the simplicity of a circulating electrolyte such as sulfuric acid with regard to cooling and water control, this electrolyte is more attractive than a solid polymer electrolyte when using direct methanol–air fuel cells for road transportation. Additionally, the automatic separation of carbon dioxide already noted eases the engineering problems considerably.

To date, the catalysts selected for either the fuel or the air electrode have been tested and operated only on a small scale. There has been little or no scale-up to practical fuel-cell sizes. Preliminary scale-up to about 10 cm × 10 cm at Shell Research in the 1970s using the then best catalyst technology (carbon-fibre-based) did not indicate any adverse effects on the performance of the fuel electrode.

A suitable fuel monitoring device must be incorporated in a practical fuel-cell stack to ensure that the fuel level remains acceptable [104]. Also, the system must be designed to ensure that losses in auxiliaries are minimized. For a direct methanol–air fuel cell using an acid electrolyte, many of these requirements have still to be resolved since no sizeable unit has been built for almost 20 years. In fact, the largest such fuel cell ever constructed was a 300-W unit which was built and operated at Shell Research in 1965. Nevertheless, there is much to be learned from the extensive work that has been performed in recent

years on the engineering of fuel cells with phosphoric acid or solid polymer electrolytes.

6. Economics

It is impossible at this stage of development to work out the precise cost of a direct methanol–air fuel cell and secondary battery hybrid system for electric vehicles since there are so many uncertain factors. Moreover, Government policy will clearly play a role in the economics, especially with respect to the environmental advantages of fuel-cell-powered vehicles, and the taxation position between methanol and gasoline (e.g., will methanol be taxed on the basis of volume or calorific value?). In fact, the revived impetus to develop fuel cells came about because of the actions of legislators in response to environmental concerns, e.g., the plan to introduce zero-emission vehicles in California [7].

Such uncertainties, together with the substantial improvements in catalytic electrode performance that are required for the successful development of vehicles powered by methanol–air fuel cells, render it premature to conduct a detailed analysis of the economics involved. Hypothetical calculations have been made [105] of the efficiencies expected from the vehicles in comparison with internal-combustion and external-combustion engined equivalents. These studies indicated that, in city driving, the fuel-cell vehicle would be three times as efficient as an internal-combustion powered vehicle, and twice as efficient as an external-combustion powered vehicle.

In our opinion, any fuel cell—be it for stationary or mobile applications—must do everything that its conventional power source counterpart does, and indeed better at the same cost or lower, for it to become a commercial success. Such success must not rely on initiatives and concessions from legislators and other Government agencies.

7. Future work

It is quite clear that for the direct methanol–air fuel cell to be a serious contender as a power source for electric vehicles, substantial improvements will have to be achieved in the performance of the catalysts for both the fuel and the air electrodes. These goals may be achieved through research in the following areas.

7.1. Electrolyte technology

Methanol oxidation in phosphoric acid electrolyte has received little attention. To date, most of the studies have concentrated on temperatures below 100°C and the results have not been promising because of the poisoning effect of acid radicals and the relatively poor ionic conductivity of

the acid. Given the immense amount of work which has been undertaken on hydrogen–air phosphoric acid fuel cells for stationary applications, it would be very short-sighted not to try and benefit from the progress which has been achieved. Thus, the development of phosphoric acid technology for gaseous methanol feedstock might prove fruitful. It should be noted that some limited experiments have been performed at high temperatures (120–205°C) in this acid [43,44]. Whereas the results were not encouraging at 120°C, reasonable current densities were obtained at 205°C. At the latter temperature, the self-poisoning effects discussed earlier may be less severe—certainly, in sulfuric acid, the decay of activity with time that arises from poisoning by organic fragments of methanol was lower as the operating temperature was increased. This strategy would require the development of an optimized gas-diffusion electrode for methanol vapour and could draw upon the expertise gained in the USA and elsewhere on high-temperature electrodes for gaseous fuels.

With phosphoric acid at high temperatures, there may well be problems with the use of chelates as air-electrode catalysts since the stability of these compounds may be poor under such operating conditions. Of course, such a problem may not be so severe if the benefits of high-temperature operation of the fuel electrode are sufficiently large. In such circumstances, it may be commercially allowable to use platinum-based catalysts for the air electrode. The difficulty then would be to prevent the platinum recrystallization which would arise from the on/off operation of the fuel cell in transportation applications.

On the engineering side, particularly if platinum-based air electrodes are used, some consideration would have to be given to minimizing or preventing the diffusion of methanol to the platinum cathode. At elevated temperatures (e.g., 205°C), both chemical oxidative and evaporative losses of methanol could be severe.

Both low-and high-temperature cells may also be possible via use of solid polymer acid electrolytes (SPEs). Some promising results have been observed with SPEs [50–53] and there are research groups actively working on these materials. Nevertheless, the associated engineering problems should not be underestimated. As there have been no reports of the construction of direct methanol power systems using SPEs, the practicality of such systems has still to be demonstrated. It is possible that the problem of methanol crossover to the air electrode, which is worse when the ionic conductivity of the electrolyte is best (highly hydrated protons), may well prove intractable. Other solid electrolytes, such as partially hydrated inorganic salts, may hold some promise for high-temperature operation [106].

7.2. Catalyst optimization and scale-up

The most active catalysts for methanol electro-oxidation catalysts reported to date, i.e., noble-metal alloys supported on carbon-fibre paper or other graphitized carbon

supports, require further improvement. There is room for an increase in the dispersion of the metal alloy by at least a factor of two before the fall-off in activity becomes dictated by the structure sensitivity of the methanol oxidation reaction. Better dispersion may be achieved by the development of an effective method of bimetallic cation exchange with the carbon surface, e.g., sequential ion exchange may prove rewarding. Also, it has been shown [107] that the stereochemistry of the complex platinum salts used in catalyst preparation can play a role in determining the electrochemical activity, e.g., whether $Pt(NH_3)_2$ $(NO_2)_2$ is *cis* or *trans* in configuration when used with $RuNO(NO_3)_x$ for the preparation of active platinum–ruthenium catalysts.

Despite the fact that platinum–tin catalysts are among the most active for methanol electro-oxidation, there have been no reports of such a catalyst supported on carbon that compares favourably with platinum–ruthenium. The gains in activity by improving platinum–tin dispersion (e.g., by supporting on carbon), are potentially as high, if not higher, than those for platinum–ruthenium on carbon paper catalysts.

Although CSIRO used a platinum-ruthenium-tin catalyst in a working methanol–air fuel cell for telecommunications systems during the early 1970s [58,108,109], the development of trimetallic catalysts has been largely neglected. This is perhaps because it has not been conclusively established how the various promoters of platinum function. If promoters exist that have differing, but positive, promoting actions, then judicious combinations of them with platinum might lead to higher activities than those obtained with bimetallics. It is interesting to note that three-component, platinum-based, reforming catalysts have been investigated for gas-phase reactions. Hamnett and Troughton [110] have suggested two forms of promotion, namely, modification of platinum by a second metal to enhance the adsorption of OH species and modification by metals which can be leached out to produce highly roughened, active, platinum surfaces. A combination of these two effects in a bimetallic catalyst may prove advantageous. The most exciting route to the discovery of more active catalysts for air and fuel electrodes could be the application of the combinatorial catalysis techniques discussed in Section 4.3.

Many workers have considered that the origin of the high activity of platinum-on-carbon-paper catalysts arises, at least in part, from the interaction which occurs between platinum and carbon to cause a modification of the surface properties of the platinum. Greater attention should be paid to determining the extent to which variation of the carbon support influences the effectiveness of platinum catalysts, or for that matter bimetallic catalysts. Such studies should be linked to work on the characterization of the carbon supports.

It must not be forgotten that the published studies of fuel and air electrode catalysts have been concerned with small-scale laboratory tests of activity and stability. There will undoubtedly be problems with scaling-up such catalytic electrodes to full size (e.g., 25 cm × 25 cm), e.g., conductivity of carbon substrate, geometry of electrodes. Thus, research should commence into clarifying the magnitude of such difficulties and devising appropriate remedial strategies.

With respect to the air electrode, the major question is: noble or non-noble metal catalyst? At this stage, it is inadvisable to concentrate on one to the exclusion of the other—too many questions remain unanswered. In the USA, considerable effort has been devoted to improving the activity and long-term stability of platinum-based air electrodes, admittedly with a different goal in mind, viz., a practical fuel cell for stationary applications. For electric vehicles, the main concern is the stability of platinum catalysts over long periods under on/off operation. It would be helpful to have more data on the magnitude of the problem associated with deactivation of platinum under these conditions and what are the real benefits of the various alloying strategies under consideration. The impressive progress made by Ballard Power Systems with transportation fuel cells using hydrogen or reformed hydrocarbons should help to bridge this gap in knowledge.

In the case of chelate and other polymeric catalysts, the interaction between carbon and the catalyst that occurs during heat treatment can produce large increases in activity and long-term stability. A detailed understanding of the processes which occur during heat treatment has still to be obtained. Also, it is necessary to examine the influence of different carbons and other conducting supports on the heat-treatment effect. Equally importantly, scale-up techniques need to be devised in order to produce practical air electrodes based on such catalysts. Finally, with respect to the possibility of using non-noble metal fuel electrocatalysts, Parsons and van der Noot [28] have suggested metal porphyrins since these compounds offer the possibility of tailoring the catalyst towards the specific reaction of interest in relation to its ability to adsorb carbonaceous species. Also, it could be possible to prepare noble-metal catalysts with small, perhaps trigonal, clusters of platinum atoms and thus create an ideal geometrical site for the oxidation of methanol.

8. Conclusions

An evaluation has been made of the status and prospects of direct methanol–air fuel cells for road transportation. This has not been an easy task, since there are no such fuel cells in operation, or even being built and tested. Thus, the approach has been to outline the history, the problems and the progress, as well as to highlight those areas where advances are required before such a fuel cell becomes a practicable proposition. In the main, the problems are

electrocatalytic, and are indeed immense. Nevertheless, there is much scope for improvement—certainly with respect to enhancing the performance of the catalyst used for methanol oxidation. Those areas where significant further progress is expected and where future work should be concentrated have been identified. Effective solutions to the present problems could be aided by more effective participation of the great talent residing in the heterogenous catalysis community. The reward for success is high, since a direct fuel cell offers the most practical means for powering electric vehicles from all points of view.

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