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Aspects of the anodic oxidation of methanol

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Abstract

This paper describes some aspects of recent investigations into the anodic oxidation of methanol. Methanol has long been proposed as an anode fuel for a fuel cell, chiefly because of its ease of carriage, distribution and manipulation. However, methanol is very much more difficult to oxidise anodically than hydrogen, the more conventional anode fuel, and this has hampered development of commercial direct methanol fuel cells. Platinum–ruthenium catalysts are the most active discovered to date. Some advances in electrocatalysis of the methanol reaction by non-noble materials are discussed. © 1997 Elsevier Science B.V.

Keywords: Methanol fuel cell; Platinum–ruthenium catalyst; Fuel cell

1. Introduction

Fuel cells constitute an important method of converting chemical energy into electricity directly, without the necessity for combustion or generation of a heat engine. The development has been slow over a long period, and most research has been devoted to the hydrogen-fuelled cell. Hydrogen has the benefit of being clean, and on a suitable electrocatalyst, highly reversible. The high exchange current densities that can be achieved from hydrogen on the platinum group metals, particularly platinum and palladium, make these the most suitable electrocatalytic materials for the fuel cell anode in acidic electrolytes. In alkaline electrolytes, where potential corrosion of the catalyst is less important, electrocatalysts which are passive towards corrosion can be employed, and the Bacon cell [1,2] used nickel for this purpose. For an electric vehicle, the fuel cell seems the ideal power source — electric power from a battery source, but with no lengthy recharging period. Recharging a fuel cell involves refilling of the fuel reservoir, as with a combustion engine. The use of hydrogen, however, poses several difficulties here. Hydrogen can be carried on board as a compressed gas, cryostatically as a liquid, or in the form of a hydride. Alternatively, a carbonaceous fuel can be carried on board, and converted to hydrogen using a reformer when required. Such a carbonaceous fuel would sensibly be methanol, since it can be carried easily in liquid form (the boiling point is 65°C). Reforming methanol produces hydrogen and carbon monoxide providing a possible route to a methanol powered fuel cell (the indirect methanol fuel cell), since this essentially uses the hydrogen anode. For many applications such as transport, this approach is probably impracticable, and the direct methanol fuel cell provides the attractive, if difficult, alternative. One of the main difficulties with this indirect methanol fuel cell is the fact that carbon monoxide is also produced by the reformer, and this

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gas must be eliminated to prevent poisoning of the electrocatalysts, or the hydrogen fuel cell powered by this route must be tolerant of CO.

Methanol on the other hand, is itself an anodically oxidisable fuel, and the efficiency of fuel usage can in principle be improved if the reforming step can be eliminated. The need to develop the direct methanol fuel cell is thus recognised, particularly as the prime power source for electrically driven vehicles. Methanol has long been proposed as an anode fuel for a fuel cell, chiefly because of its ease of carriage, distribution and manipulation. However, methanol is very much more difficult to oxidise anodically than hydrogen, the more conventional anode fuel, and this has hampered development of commercial fuel cells. Much of this difficulty arises because the methanol oxidation reaction is highly irreversible, even on the best catalysts, and it consequently requires significant overpotentials to drive the reaction at a significant rate. The objective is to generate a low temperature fuel cell, particularly for transport power, where high temperatures are not required.

The complete anodic oxidation of methanol is described by:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad (1)$$

The requirements of the electrocatalysts can be specified simply. The first requirement is a high electrocatalytic activity for the full six-electron transfer reaction. This electrocatalytic activity can only be achieved if the material has a high electronic conductivity. The fact that CO_2 is produced implies that the electrolyte must be acidic; two electrolytes are proposed to fulfil this: aqueous sulphuric acid (at $T<\sim 80^\circ C$) or the solid polymer electrolyte Nafion™ (at $T\approx 100^\circ C$). The electrocatalyst must be stable towards these strongly acidic electrolytes, both chemically and structurally. Chemical stability can be achieved thermodynamically (the catalyst is "immune" from corrosion), for which only noble metals are suitable, or it can be achieved using the passive state, where the term "passive" in this context means passive towards corrosion. Finally, because of the fact that the six electron transfer reaction (1) must involve several intermediate steps, the electrocatalyst should be tolerant towards poisoning from the intermediates formed during the reaction.

2. Mechanism of the anodic oxidation of methanol

Many mechanisms have been proposed for the anodic oxidation of methanol [2–12]. The full anodic reaction to yield carbon dioxide (reaction 1) involves a six-electron oxidation of the carbon atom. The thermodynamic equilibrium potential for reaction 1 calculated from the standard chemical potentials at 25°C tabulated by Pourbaix [13] is 0.03 V (SHE). However, because of the number of electrons involved, equilibrium is not readily realisable, even on the best electrocatalysts so far devised. Anodic oxidation thus involves a number of steps, all of which produce intermediate products. Some of these intermediate products are themselves relatively stable compounds. Thus, it is expected that formaldehyde, formic acid and carbon monoxide would be formed as intermediates, and these may well acquire sufficient stability for further reaction to be difficult. It is well to consider these reactions and their standard thermodynamics, in an attempt to isolate those steps which may prove difficult, at least on thermodynamic grounds.

Equilibrium may be considered between methanol and any of a number of appropriate intermediate stable phases, or between the stable phases themselves, as shown in Table 1; the table lists the standard free energies of reaction and the standard equilibrium potentials for the reactions. A succession of anodic reactions involving the stable phases can thus be proposed as a mechanism for the full oxidation of

Table 1
Standard thermodynamics of the anodic oxidation of methanol via stable compounds at 25°C, using standard states of 1 atm for gases (CO, CO_2) and 1 mol dm^{-3} for dissolved components (CH_3OH, $HCHO$, HCO_2H). Calculated from the standard chemical potentials given by Pourbaix [13]

Reaction	ΔG^0 (kJ mol^{-1})	E^0 (V, SHE)
$CH_3OH \rightarrow HCHO + 2H^+ + 2e^-$	−44.8	+0.232
$CH_3OH \rightarrow CO + 4H^+ + 4e^-$	−37.2	+0.096
$CH_3OH + H_2O \rightarrow HCO_2H + 4H^+ + 4e^-$	−55.6	+0.144
$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	−17.3	+0.030
$HCHO \rightarrow CO + 2H^+ + 2e^-$	+7.6	−0.039
$HCHO + H_2O \rightarrow HCO_2H + 2H^+ + 2e^-$	−10.8	+0.056
$HCHO + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$	+27.5	−0.071
$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$	+19.9	−0.103
$HCO_2H \rightarrow CO_2 + 2H^+ + 2e^-$	+38.3	−0.198

the fuel to CO_2 (with a and b below being alternative oxidative steps) as follows:

$$CH_3OH \rightarrow HCHO + 2H^+ + 2e^- \quad (2)$$

$$HCHO + H_2O \rightarrow HCO_2H + 2H^+ + 2e^- \quad (3a)$$

$$HCHO \rightarrow CO + 2H^+ + 2e^- \quad (3b)$$

$$HCO_2H \rightarrow CO_2 + 2H^+ + 2e^- \quad (4a)$$

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad (4b)$$

In the above description of the mechanism, the adsorption of the various reacting species is taken for granted, since initial adsorption is necessary for any interfacial reaction. Such a mechanism is likely to be too facile to describe the reaction in full. Nevertheless, it serves to emphasize some chemical thermodynamics of the system. The lowest of the standard equilibrium potentials involving methanol itself is the CH_3OH/CO_2 reaction, the overall reaction. Other reactions involve considerably higher equilibrium potentials, particularly the $CH_3OH/HCHO$ reaction (the highest value listed in Table 1). It is thus clear that if the mechanism of anodic oxidation were to go through this sequence of relatively stable intermediate products, the first step involving formation of formaldehyde, would be thermodynamically the most difficult. Some 0.2 V overpotential (relative to the equilibrium potential for the CH_3OH/CO_2 reaction) would be necessary simply to allow this reaction (2) to equilibrate. The successful running of the methanol-fed anode is in fact hampered largely by the fact that an anodic overpotential of some 0.3–0.4 V is required to drive the anode at a significant rate; this prominent feature of the reaction was displayed in the work of Hampson et al. [14] at ca. 0.55 V (SHE). Despite the thermodynamics of reaction 2, the precise origin of this overpotential is unknown; a similar overpotential barrier is experienced during anodic oxidation of other carbonaceous fuels such as formic acid [15]. This observation precludes poisoning by early stage intermediates as being the exclusive reason for the overpotential barrier. The sequence 2→3a or 3b→4a or 4b represents a possible mechanism based only on intermediates, which are relatively stable and which can exist as separate entities without a stabilising surface. There have been many discussions in the literature [10,16,17] as to whether these intermediates form in parallel with the oxidation to CO_2, essentially as side reactions (as discussed by Breiter [6]), or whether they are formed as intermediates in the CO_2 production (series reactions), but with no suitable conclusion. The implications of the formation of these relatively stable oxidation states as intermediates in series or in parallel are clear. By running in parallel, the anodic reaction is no longer 100% current efficient, since some of the oxidation product would escape the electrode in an oxidation state lower than CO_2. By running in series, such stable oxidation states of carbon must add to the overpotential required to drive the reaction. The above mechanism, based only on the stability of the intermediates, is in broad agreement with Breiter's work [6], except that Breiter allowed for a dual path reaction, both ultimately resulting in production of carbon dioxide. It is however, quite different from that of Bagotsky and Vassilyev [4], where only unstable adsorbed intermediates are formed:

$$CH_3OH + Pt \rightarrow Pt\text{-}COH + 3H^+ + 3e^- \quad (5)$$

$$H_2O + Pt \rightarrow Pt\text{-}OH + H^+ + e^- \quad (6)$$

$$Pt\text{-}COH + Pt\text{-}OH \rightarrow Pt\text{-}CO + H_2O + Pt \quad (7)$$

$$Pt\text{-}CO + Pt\text{-}OH \rightarrow Pt\text{-}COOH + H^+ + e^- \quad (8)$$

$$Pt\text{-}COOH + Pt\text{-}OH \rightarrow CO_2 + H_2O + 2Pt \quad (9)$$

In this process, step 6 precedes each of steps 7, 8 and 9 in providing the electron transfer, and carbon is then oxidised by the adsorbed OH radical.

Other features of this complex electrochemical mechanism concern possible surface intermediates acting as poisons for the electrocatalyst, hence retarding the overall reaction. It is generally agreed that there is some poison for the anode electrocatalyst, but the identity of the poisoning species is uncertain. The poison is commonly perceived as an adsorbed layer of CO, CHO or COH formed as intermediates in the anodic reaction, these species being chemisorbed to the platinum surface and difficult to remove [4–12,14–21]. The curious feature of these adsorbed species in terms of being poisons is that they are also expected to be intermediates in the anodic reaction to give CO_2. Their accumulation on the catalyst surface to high coverage may imply that their further oxidation and/or desorption is the slow step in the reaction [4,5,7,8]. If these intermediates function exclusively as poisons (implying parallel path reactions), their high steady-state coverage over the electrocatalyst implies a smaller remaining surface area available for the reaction to CO_2. Other steps such as C–H bond scission are also proposed as rate-determining [10,12,17]. These issues remain to be resolved.

The most successful anode catalyst for the methanol fuel cell is a mixture of platinum and ruthenium, the two metals generally being codeposited from solution. Platinum alone is a poor electrocatalyst, because it is poisoned severely during anodic oxidation of methanol [22,23]. One of the proposed roles for ruthenium used in conjunction with platinum as an anode electrocatalyst for methanol is its ability to aid the desorption of the catalyst poison from the platinum surface [15,24], thereby increasing the effective surface area available for the oxidation reaction to proceed. For optimum resistance to poisoning by this route, it is apparent that the ruthenium should be in solid solution with the platinum; such a solid solution is consistent with the high solid solubility of ruthenium in platinum [25]. The optimum ratio of Pt to Ru in these alloy electrocatalysts has been variously cited as between 9:1 and 1:1 [23,26–28]. The enhanced desorption from the surface as imparted by ruthenium can be envisaged as follows:

$$CH_3OH + Pt \rightarrow (Pt)CH_2OH + H^+ + e^- \qquad (10)$$

$$(Pt)CH_2OH + Ru \rightarrow (Ru)(Pt)CHOH + H^+ + e- \qquad (11)$$

$$(Ru)(Pt)CHOH + Pt \rightarrow (Ru)(Pt)_2COH + H^+ + e^- \qquad (12)$$

$$(Ru)(Pt)_2COH + H_2O \xrightarrow[\text{multiple steps}]{} CO_2 + 3H^+ + 3e^- + Ru + 2Pt \qquad (13)$$

$$(Ru)(Pt)_2COH \rightarrow (Ru)\cdots CO + H^+ + e^- \qquad (14)$$

The metal atoms in parentheses are surface catalyst atoms onto which the oxidising carbon atom of the reacting fragment is adsorbed. Here the reaction passes through a series of adsorbed intermediates via successive deprotonation steps (steps 10–14), one of which is the COH group (formed in step 12), pyramidally bonded over by three surface catalyst atoms. If Ru aids the desorption as proposed, then this mechanism would imply that a Pt/Ru atomic ratio of 2 could be optimum. Such a notion, however, would require that the solid solution of Ru in Pt has a perfect structural distribution of Ru in Pt. Solid solution alloy structures do not generally acquire such perfection; random clustering occurs and the optimum composition for such a mechanism becomes difficult to predict, even for a known reaction mechanism. In fact, because of the many features of the mechanism which remain poorly understood, the role of ruthenium in promoting the reaction is also not straight forward.

3. Anodic reaction of methanol on Pt/Ru

Electrodes were made from Pt/Ru on carbon (Johnson–Matthey) using a derivatised carbon cloth (Zoltek) and polytetrafluoroethylene (ICI GP-1) suspended in tetrahydrofuran. After applying the suspension to the cloth, it was dried, pressed and sintered to produce a circular porous electrode of diameter 2 cm (area 3.14 cm^2). Because, some of these electrodes proved fragile when bent, some formulations included 15% by weight of chopped carbon fibre: this provided significant improvement in mechanical strength. Electrodes were then tested in sulphuric acid electrolyte (concentration 1.5 $mol\ dm^{-3}$) using methanol as fuel. The fuel was either dissolved in the electrolyte (concentration 2.5 or 5 $mol\ dm^{-3}$), or it was supplied as a vapour. In the latter case, the electrochemical cell was fitted with a gas compartment so that the gas-fed electrode formed a membrane between the fuel vapour and the electrolyte. For a vapour-fed fuel electrode, the methanol was contained in an external reservoir and a stream of pure argon or nitrogen was passed through. The methanol saturated gas stream was then heated and fed into the gas compartment of the electrochemical cell. Alternatively, some measurements used pure methanol vapour from a boiling reservoir, with the system held at 67°C, 2° above the boiling point of the fuel. The experiments were run at temperatures in the range 60–67°C. Electrochemical measurements were made potentiostatically or galvanostatically with the control parameter held constant for 200 s or 250 s; this was in order to determine a steady-state reaction rate.

Potentials were measured against a remote saturated calomel or mercury/mercurous sulphate reference electrode and are presented below against the 25°C standard hydrogen electrode (SHE) scale. The reference electrode was maintained in a side-arm to the cell at ambient temperature, irrespective of the

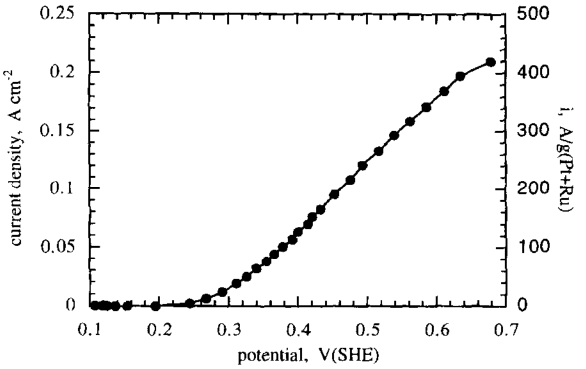

Fig. 1. Anodic oxidation of methanol vapour in a nitrogen carrier gas at 65°C over a platinum/ruthenium catalyst in 1.5 mol dm^{-3} H_2SO_4. The derivatised electrode was made from <0.5 mg cm^{-2} (Pt+Ru) as 66 wt% Pt, 34 wt% Ru, and was reinforced with 15 wt% carbon fibre.

temperature of the working electrolyte. The data were not corrected for the ohmic potential drop between the working electrode and the Luggin capillary tip. Such a correction, if made, would include all the ohmic components of the working electrode, including that in the electrolyte as well as those associated with the electrode itself and the electrical contacts. However, linearity in the voltammograms at high current density implies ohmic control, and the approximate resistance can be determined from the gradient of those linear regimes. For a 1 mm spacing between the working electrode and the Luggin capillary tip, the ohmic resistance in the electrolyte alone (1.5 mol dm^{-3} H_2SO_4, 65°C) is 42 mΩ, much less than that given by the gradients of the high current linear regions below. This implies that the electrode itself carries significant ohmic losses, either in the electrolyte within the porous matrix, or as electronic resistances within the electrode structure and contacts.

Fig. 1 shows the reactivity of methanol vapour at 65°C on Pt/Ru (atom ratio 1:1). It is apparent that there is an overpotential barrier of some 0.25–0.3 V before the anodic oxidation reaction starts to occur at a significant rate. This overpotential barrier can be observed in the results of many others as noted above. The reaction rate rises roughly linearly for E >0.35 V (SHE), showing a significantly high ohmic resistance in the electrode system: the gradient of the linear region of Fig. 1 gives a resistance of ca. 0.54 Ω for the 2 cm diameter electrode. Also plotted on the same graph is the performance of the electrode expressed as current per unit mass of total noble metal (Pt+Ru). At a current density of 100 mA cm^{-2}, the anode potential is 0.47 V (SHE) (uncorrected for the ohmic potential drop) and the usage of total noble metal catalyst (Pt+Ru) gives 200 A g^{-1}. Expressed in terms of the platinum content only, the figure is 304 A g^{-1} (Pt).

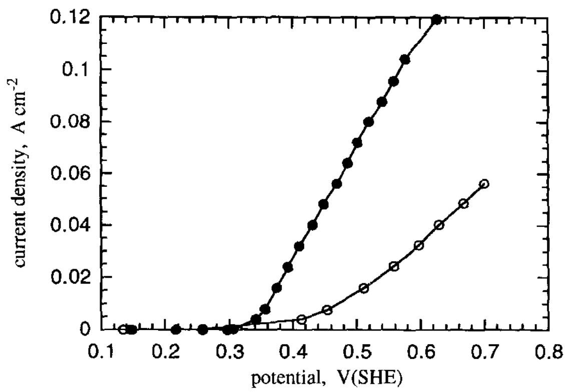

Fig. 2. Anodic oxidation of 5 mol dm^{-3} methanol (white circles) and 5 mol dm^{-3} formic acid (black circles) in 1.5 mol dm^{-3} H_2SO_4 at 58°C using 0.84 mg cm^{-2} (Pt+Ru).

The effect of bypassing some of the steps involved in the mechanisms in reactions 2–14 above can be seen by comparing the rate of reaction of methanol and of formic acid, shown in Fig. 2. To maintain comparable concentrations, the fuels were dissolved in the electrolyte. This particular electrode was of modest performance; nevertheless, the comparison can still be drawn. Formic acid reacts significantly faster than methanol, as expected. Because methanol is oxidised by six electrons and formic acid by only two electrons, the relative reaction rate per mole of formic acid to that of methanol is even greater. What is nevertheless surprising, is that the ca. 0.3 V overpotential required to drive the anodic reaction at a significant rate is common to both fuels, irrespective of how fast the reaction occurs at higher overpotentials. This suggests that the initial oxidation of methanol to formaldehyde is not the exclusive reason for this initiating overpotential, as suggested by Table 1. Indeed, Table 1 shows that the standard equilibrium potential between HCO_2H and CO_2 is low. Although the anodic oxidation of formic acid is more rapid, the initial activation overpotential is not surmounted in comparison with the anodic oxidation of methanol.

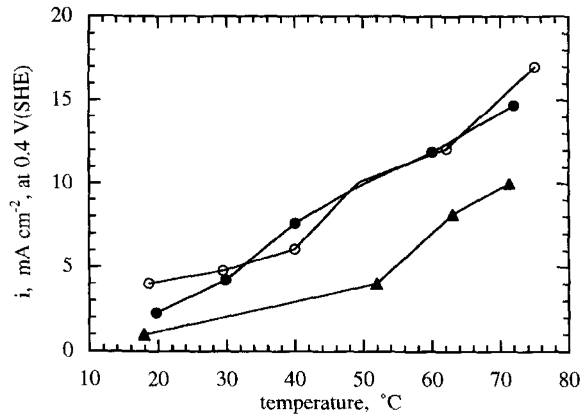

Fig. 3. Anodic oxidation of methanol vapour in an argon carrier gas in 1.5 mol dm^{-3} H_2SO_4 at 0.4 V (SHE) as a function of temperature showing the effect of silicotungstic acid ($H_4SiW_{12}O_{38}$) dissolved in the electrolyte. The anode catalyst carried 0.88 mg cm^{-2} (Pt+Ru). Triangles: no $H_4SiW_{12}O_{38}$. White circles: rate after 200 s. Black circles: rate after 48 h.

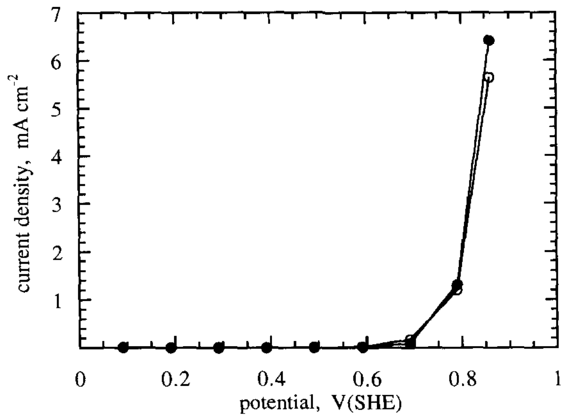

Fig. 4. Anodic polarisation of tungsten carbide in 1.5 mol dm^{-3} H_2SO_4 at 60°C without methanol vapour (black circles) and with 5 mol dm^{-3} methanol dissolved in the electrolyte (white circles). Where no white data points are shown they overlap with the black ones.

Some activating effects of electrolyte additions can be achieved. Fig. 3 shows the acceleration of the anodic oxidation of methanol, when silicotungstic acid ($H_4SiW_{12}O_{38}$) was added to the electrolyte (1.5 mol dm^{-3} H_2SO_4). In Fig. 3, the data are presented as the anodic current density measured at 0.4 V (SHE) as a function of temperature. The presence of 10 mmol dm^{-3} silicotungstic acid accelerates the reaction rate by around 50 and 100%. The reaction rate enhancement is not a strong one; nevertheless, the effect was found to be permanent, with no reduction in the promoting effect after exposure for 48 h.

4. Anodic oxidation of methanol using base electrocatalysts

Base electrocatalysts have been suggested earlier for the direct methanol fuel cell. Electrocatalysts made from base materials must be able to resist the corrosive action of the acidic electrolytes used. Acidic electrolytes are a requirement for the low temperature direct methanol fuel cell, chiefly in order to reject CO_2, which would dissolve in neutral or alkaline solution. Since base metallic materials are themselves thermodynamically unstable in acidic solutions, the requirement for any base electrocatalyst is that it is passive towards corrosion. Tungsten and molybdenum carbides have been shown to have some electrocatalytic activity towards the methanol oxidation reaction [29], and a hydrogen fuelled cell stack has been built with a tungsten carbide anode using phosphoric acid as electrolyte, and operating at 150°C [30].

We have synthesized tungsten carbide by reduction of tungsten oxide in a gas stream of methane and hydrogen at 823°C. This material, when made into an electrode suitable for anodic oxidation of methanol, showed no detectable electrocatalytic activity, as shown in Fig. 4. In this case, the cell was run at 60°C using 5 mol dm^{-3} CH_3OH dissolved in the electrolyte, and the figure shows the comparison between currents recorded with and without fuel. In the absence of the fuel, the anodic currents represent the anodic oxidation of the electrode itself. Similar experiments run using commercially acquired tungsten carbide also showed no electrocatalytic activity. The corrosion current densities were, however low, and the materials showed significant passivity towards corrosion. The results shown in Fig. 4 are those measured after 250 s at constant potential, and the anodic currents were still slowly falling at that stage, indicating continuing passivation. The result is in conflict with the work of Bronoel [29], and probably reflects the requirement for specific surface composition and geometry in order to achieve electrocatalytic activity.

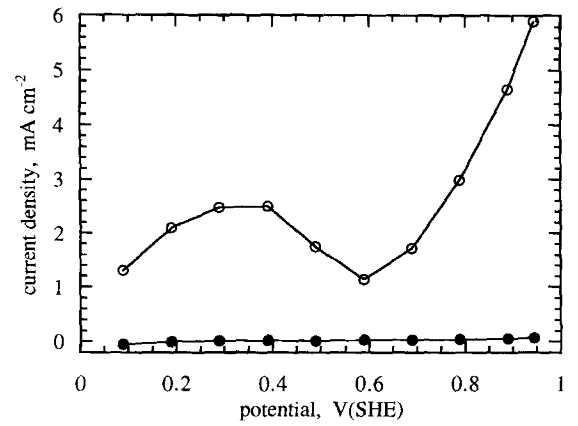

Fig. 5. Anodic oxidation of pure methanol vapour (white circles) at 67°C over carburised nickel tungsten of unit mole ratio in 1.5 mol dm^{-3} H_2SO_4. Black circles: polarisation of the catalyst without added methanol.

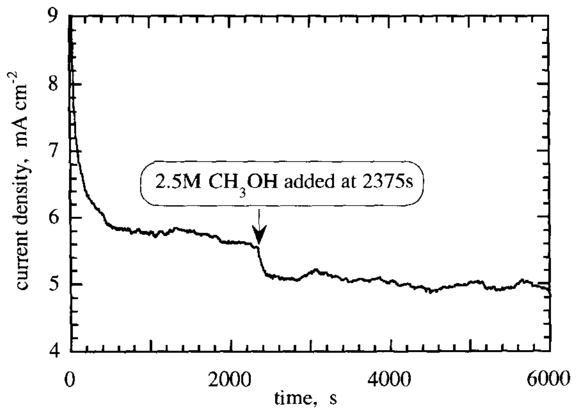

Fig. 6. Effect of adding methanol to 2.5 mol dm^{-3} whilst polarising carburised cobalt tungsten (of unit mole ratio) at 0.520 V (SHE) in 1.5 mol dm^{-3} H_2SO_4 at 60°C. Addition of the methanol after 2375 s shows a decrease in anodic current flowing.

A similar material, but using a mixture of nickel and tungsten in the mole ratio of 1:1 was also made [31]. In this case, the starting material was nickel tungstate prepared by mixing equimolar proportions of nickel nitrate and sodium tungstate; after drying, the tungstate was reduced in a methane/hydrogen atmosphere at 823°C. The results are shown in Fig. 5. This material showed a very low corrosion rate in the sulphuric acid electrolyte (at 67°C), demonstrated by the low passive current densities measured in the absence of methanol. At room temperature, the corrosion rate was even lower. The presence of methanol gave rise to a much higher anodic current density, indicating electrocatalytic activity towards the anodic oxidation of methanol, also shown in Fig. 5. The material showed a high degree of passivity towards corrosion and a modest electrocatalytic activity towards methanol oxidation up to a potential of ~0.6 V (SHE). At potentials higher than this, some transpassivation of the passive state occurred, and the corrosion currents increased. It is to be noted with interest that the rate of anodic oxidation of methanol is also enhanced in this transpassive region. Clearly, this passive electrocatalyst is more catalytically active if the surface is transpassivated. The high potential region can unfortunately be of little interest in the context of fuel cells, because the corrosion rate of the catalyst is higher here and because the potential is too high to be considered as an anode in a fuel cell.

The electrocatalytic activity shown in Fig. 5 for the carburised Ni/W material was not shown by a similar preparation using cobalt in place of nickel. This material, made by reduction of cobalt tungstate showed a high corrosion rate in sulphuric acid at 60°C; the result is shown in Fig. 6 in terms of the current density measured at constant potential (0.520 V (SHE)) as a function of time. Initially, the electrode was polarised in sulphuric acid without added fuel. The corrosion current decays, initially rapidly, but even after almost 40 min, is still high. Addition of methanol to the electrolyte at 2375 s incurred a reduction in the anodic current flowing. This phenomenon means that methanol acts as a corrosion inhibitor for this material, although because the reduction in anodic current is small, the corrosion inihibition is small. No electrocatalytic activity of the material towards the anodic oxidation of methanol could be detected. If any anodic oxidation of the fuel does occur on this electrode, the current due to this is swamped by the corrosion current. This material is very different in response from the nickel based material described in Fig. 5.

An analogue of this type of material was also prepared using ruthenium tungstate to generate an electrode from reduced ruthenium and tungsten in an atomic ratio Ru/W≈1. The results from experi-

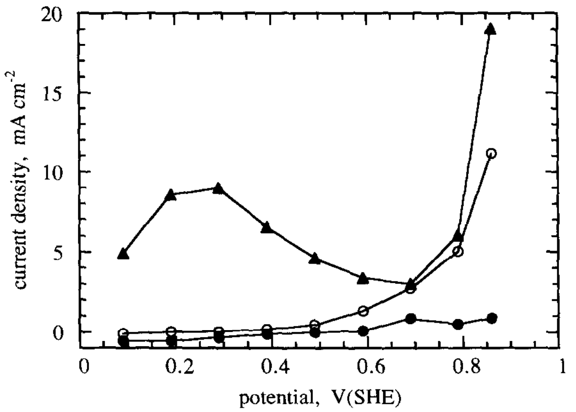

Fig. 7. Polarisation of carburised ruthenium tungsten (of unit mole ratio) in 1.5 mol dm^{-3} H_2SO_4 at 67°C showing the presence of pure methanol vapour as fuel (white circles) and pure hydrogen as fuel (triangles). Black circles: polarisation of the catalyst with no fuel.

ments with this electrode are shown in Fig. 7. This material was also very passive, up to a potential of ca. 0.6 V (SHE), above which significant transpassivation occurred. This electrocatalyst showed very low methanol oxidation currents at the lower potentials. Only above ca. 0.6 V (SHE) could a reasonable methanol oxidation current be observed, and this is not large relative to the catalyst corrosion current. In Fig. 5, it was shown that the nickel based catalyst (carburised Ni/W) showed a minimum potential of 0.3 V (SHE) for methanol oxidation at 2.5 mA cm^{-2}. The lowest potential for which the ruthenium catalyst shows a methanol oxidation current of 2.5 mA cm^{-2} is 0.7 V (SHE), a much higher potential. Although the electrode manufacture exhibited some irreproducibility, and scatter from one electrode to another, the potential at which methanol oxidation occurs at a rate comparable between these two catalysts is much higher for the ruthenium based material: it is an inferior electrocatalyst. Fig. 7 also shows the anodic oxidation of gaseous hydrogen at 67°C. A maximum rate of 9 mA cm^{-2} in the low potential regime (below the potential for transpassivation) was measured at 0.25 V (SHE): this catalyst is a weak catalyst for the hydrogen reaction. Even in the transpassive regime, for potentials above ca. 0.6 V (SHE), the excess rate of anodic reaction when fuelled with hydrogen is not great.

5. Discussion

The notion that operation of a methanol fuel cell at low temperature should approach the current and power densities exhibited by a hydrogen fuel cell has little foundation. Although the standard thermodynamic equilibrium potentials exhibited for the hydrogen electrode and the methanol electrode are very similar (Table 1 shows that the CH_3OH/CO_2 equilibrium potential (reaction 1) is only 30 mV different from that for H_2/H^+), most other features of the reactions are different. The biggest hindrance for the direct methanol anode is the ca. 0.3–0.4 V overpotential required to drive the reaction. This potential can be explained thermodynamically, by considering the fact that the methanol oxidation reaction to CO_2 involves six electrons, and thus necessarily passes through a range of intermediate steps, one of which might be the oxidation of the fuel to formaldehyde. Since, $CH_3OH/HCHO$ reaction (reaction 2) itself has an equilibrium potential, some 0.2 V higher than the CH_3OH/CO_2 reaction, a thermodynamic barrier towards the anode fuel is deduced. (Table 1 shows other high equilibrium potentials as well). However, the explanation is not so simple. The result in Fig. 2 shows that anodic oxidation of HCO_2H to CO_2 (a two electron transfer) also shows this overpotential barrier towards oxidation, and this is unlikely to be thermodynamic. The problem is thus, at least in part, one of electrocatalysis. That this is so, is evident from the fact that the data from different laboratories frequently show different values of this initial activation overpotential barrier, and indeed, the values obtained above are also variable, dependent on the catalyst. Thus for example, Fig. 1 shows this barrier to be ca. 0.25–0.3 V for the Pt/Ru catalyst, but Fig. 7 shows it to be ca. 0.6–0.7 V for the carburised Ru/W electrode. The carburised Ru/W electrocatalyst showed poor performance for methanol oxidation. The ruthenium component of the conventional Pt/Ru electrocatalyst is clearly a promoting agent for the main electrocatalyst which is platinum. Ruthenium on its own shows very poor performance; this observation is in agreement with other work [23].

Some authors have suggested that the issue is one of poisoning of the catalyst by intermediates. Vielstich [16] has argued that the production of CO_2 from methanol oxidation does not commence until at least

0.5 V overpotential has been surmounted. His argument stems from the observation that the production of CO_2 from anodic oxidation of CH_3OH is not enhanced by increasing the potential in the overpotential range 0–0.5 V. There could be many reasons for this, however, and the argument does not seem necessary or sufficient to describe the observation. Indeed, his results show that CO_2 is in fact generated at low overpotential; it is simply not increased by raising the overpotential. The issue has been contested [17]. Full analysis of the emerging gases arising from the anodic oxidation of methanol has yet to be carried out. Clearly, successful operation of the direct methanol fuel cell requires complete oxidation to CO_2.

The recent result of Hamnett's group [32,33] in producing a platinum/ruthenium alloy of high electrocatalytic performance still shows a high initial overpotential required to activate the oxidation ($<\sim$0.2 V), but not as great as that observed earlier [14]. (It is worth bearing in mind that high performance direct methanol fuel cells have to date only been achieved when the system is pressurised, both at the anode and at the cathode [34,35]). The lower overpotential for activation is commensurate with Fig. 1 which also shows some 0.25–0.3 V required activation. Fig. 5, showing the behaviour of the carburised nickel/tungsten catalyst, also displays a fairly similar low overpotential for that activation for the methanol reaction (ca. 0.3 V).

Many other catalyst promoting agents in conjunction with platinum have been proposed [26], including Bi [36], Sn [37–41], Co [42], Re, Ti, Zr, Nb, and Ta [43]. None offers the promoting effects of ruthenium towards anodic oxidation of methanol.

Base electrocatalysts for the anodic oxidation of methanol are demonstrated to be possible. The requirement for passivity is fulfilled by the carburised Ni/W material, which also showed modest anodic electrocatalytic activity. Although the synthesis and testing of this material has not yet been optimised for electrocatalytic activity, it seems unlikely that its activity will ever approach that of the platinum/ruthenium alloy, now adopted as routine in testing of the direct methanol fuel cell. Nevertheless, its behaviour warrants some attention. A carburised nickel preparation which carried no tungsten showed a large corrosion rate, and could not be used as an electrocatalyst in these acidic electrolytes even if it showed catalytic activity. The corresponding tungsten preparation, tungsten carbide, showed excellent passivity, (consistent with the phosphoric acid fuel cell which employed the material as anode [30]), but no electrocatalytic activity. The carburised nickel tungsten showed the passivity of WC but also electrocatalytic activity. Clearly, the passivity towards corrosion is imparted by the tungsten component, and the electrocatalytic activity by the nickel component. It appears that the nickel must be held in a some sort of tungsten carbide lattice, or tungsten itself is dissolved in a nickel lattice in order for the nickel component to become passive and remain so. This interesting phenomenon implies that the nickel component can be stabilised (passivated) by association with tungsten in electrolytes in which passivity would otherwise not be achieved. Tungsten is expected to be passivated in sulphuric acid according to Pourbaix; nickel is not [13]. It is also interesting to note that the maximum level of electrocatalytic activity is at potentials, where the catalyst has been transpassivated ($>\sim$ 0.65–0.75 V (SHE)). We believe that the reason for this lies in the enrichment of the surface with nickel in this transpassive regime. Since, tungsten carbide itself tends to transpassivate at these potentials, dissolution of tungsten from the catalyst surface would give some enrichment of nickel at the surface; presumably, the corrosion rate of the entire catalyst rises here, but notwithstanding that, nickel is enriched giving enhancement of the catalytic activity.

The basic mechanism of the process is sketched in Fig. 8. The intervening oxide film between the catalyst particles and the electrolyte/methanol must provide an electron conducting path for fuel oxidation to occur. Methanol is initially adsorbed onto the passivating oxide surface in order for its anodic oxidation to take place. It can then be oxidised using oxide ions obtained from the aqueous phase as shown in the reaction schemes above (e.g. reactions 2–4 or 13). Alternatively, oxide ions can in principle be taken from the passivating oxide surface, and the anion vacancies in the film thus generated, can be annihilated via the aqueous phase after desorption of the reaction products. For example, if it is imagined that CO is adsorbed to the passivating oxide surface, and the anodic reaction to CO_2 is to occur, then the following reaction scheme could describe the process:

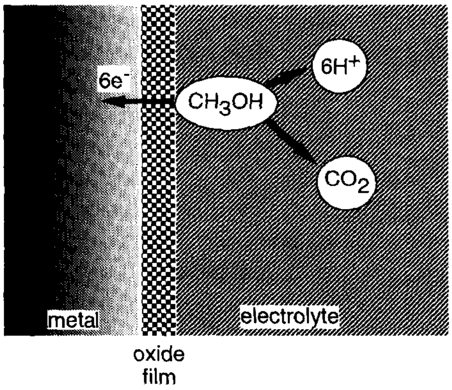

Fig. 8. Basic model for the anodic oxidation of methanol through an electrocatalytic surface generated by passivating the surface with an oxide film. The oxide film must be sufficiently conductive towards electrons.

$$CO_{ads} + MO \rightarrow CO_2 + V_O'' + 2e^- \quad (15)$$

$$V_O'' + H_2O \rightarrow MO + 2H^+ \quad (16)$$

where MO represents the oxide film and V_O'' is an oxide ion vacancy in the film. The same mechanism can be applied to any step in the reaction which requires oxide anions: the above reaction is simply an example. This mechanism is essentially similar to reactions 5–9, with the oxide anions supplied by the surface of the catalyst rather than from the solvent. Note that loss of the oxide anion from the surface by reaction 15 could alternatively be succeeded by dissolution of the associated metal cation. There is no evidence for this: the presence of methanol reduces the rate of catalyst dissolution (as shown for example in Fig. 6) [44]. The rise in rate of methanol oxidation in the transpassive region does not violate the mechanism. The corrosion current density in the transpassive region of Fig. 5 is too low to represent corrosion from a film-free surface; there is no doubt that the surface here too is covered by an oxide film, but this film is less passivating (towards anodic corrosion). Note that passive electrocatalysts have been exploited before in the Bacon cell [1]. Moreover, it is clear that the Bacon cell anodes must operate using a similar type of mechanism to that illustrated in Fig. 8, since the nickel anodes indubitably carry a passivating oxide film in the caustic electrolyte, and reaction of the fuel must occur through this.

Since, these materials are passive because of the generation of an intervening oxide film, one must regard the oxide surface as being the electrocatalyst. Its composition is at this stage unknown; however, one possibility would be that the Ni:W mole ratio in the surface approaches a value of unity, effectively providing passivity with a thin film of nickel tungstate or nickel oxide immersed in a tungstic acid matrix. In this connection, it should be noted that Tseung et al. [45,46] have synthesised electrocatalysts of high activity using platinum and tungstic acid. We note that the X-ray diffraction pattern of the carburised nickel/tungsten material shows, in addition to tungsten carbide, a set of nickel reflections which are nonetheless displaced from those describing pure nickel [44]. It seems that this may represent the distortion of the nickel lattice by incorporating dissolved tungsten. Preferential dissolution of nickel is thus a reasonable explanation of the passive electrocatalyst, providing some mixed Ni/W oxide as the stabilising passivating surface which, largely through its nickel component, provides electrocatalysis for the anodic oxidation of methanol.

Any base material considered as a potential electrocatalyst must be rendered passive by the acidic electrolyte and the potentials of anode operation. It is mainly because of this that the role of tungsten in this electro-oxidation reaction should be considered. Both oxidised and reduced tungsten, in various forms have been incorporated into fuel cell experiments [26,29,30], generally to some benefit for the reaction. This has been both as anode electrocatalyst, and as promoter for the anodic reaction. It has been used in the form of tungsten carbide as an anode in the phosphoric acid fuel cell. Whilst tungsten carbide is isoelectronic with platinum, with the implication that it may consequently show electrocatalytic activity, the experiments described above have been unable to determine electrocatalytic activity towards the methanol oxidation reaction. The reason may be that tungsten carbide is of itself expected to achieve passivity in acidic electrolytes by means of an oxide film (as WO_3 for example), and this surface can no longer be isoelectronic with platinum. For this reason, it is believed that the data of Fig. 5 describe electrocatalytic activity of the nickel component of the electrocatalyst, and not of the WC component. Nevertheless, the work of Bronoel et al. [29] ascribes electrocatalytic activity of WC itself towards methanol oxidation. The promoting of methanol oxidation by use of tungsten compounds is also exemplified by the work of Tseung et al. [45,46] in which platinum and tungsten oxide were codeposited to provide a powerful electrocatalyst towards anodic oxidation of methanol. In this case, cathodic pretreatment of the electrode, which generates tungstic acid on the surface is thought to provide the promotion of the methanol oxidation reaction. Finally, the effect of silicotungstic acid addition to the sulphuric acid electrolyte described above also provides promotion for the anodic oxidation of methanol, consistent with earlier observations using a Pt–Sn electrocatalyst [47]. This cannot be an effect of the electrolyte per se, since the concentration added (10 mmol dm^{-3} in Fig. 3) was very small relative to the sulphuric acid concentration (1.5 mol dm^{-3}). It must therefore be reasoned that the silicotungstate anion, a large Keggin unit, is adsorbed onto the Pt/Ru electrocatalyst surface and provides promotion at this level. The mode by which the reaction is promoted is not known. Nevertheless, it is expected that the tungsten bound into the Keggin unit is capable of exhibiting variable oxidation states. This phenomenon is seen clearly when aqueous solutions of silicotungstic acid are cathodised gently: the electrolyte turns blue, presumably by reduction of W(VI) to W(V). This is similar to the Pt/WO_3 electrocatalyst of Tseung [45,46], where the reduction can be alternatively viewed in terms of the labile hydrogen atom in tungstic acid, HWO_3. Finally, the effects of carburised Ni/W above are noted as modest electrocatalysts. The two features of the various tungsten materials which may provide this catalytic enhancement are its stability in acidic electrolytes over a range of potentials of interest in the operation of a fuel cell anode (by means of its essentially passive state), and its possible mixed oxidation states on the surface. Clearly, much more research into the application of tungsten-based materials needs to be carried out.

6. Conclusion

Electrocatalytic oxidation of methanol for use in a direct methanol fuel cell operates through a complex mechanism. Several relatively stable intermediates, such as formaldehyde and formic acid may be formed, which may be liberated from the electrode surface, giving an anodic current efficiency for oxidation of the fuel of <100%. There is an initial activation overpotential of some 0.2–0.55 V (depending on the electrode) required to oxidise methanol anodically at an appreciable rate. This activation barrier is one of the severe constraints on the use of methanol in the low temperature direct methanol fuel cell. Some of the intermediate reactions (such as anodic oxidation of CH_3OH to HCHO) have relatively high thermodynamic equilibrium potentials; if such a reaction is a necessary intermediate in the anodic oxidation of methanol, then the phenomenon explains the high initial activating overpotential of ca. 0.2–0.55 V required to drive the methanol fuel anode. This cannot be the entire explanation of the initiating anodic overpotential barrier, however, since it is observed that anodic oxidation of formic acid also requires a similar initiating overpotential. At least some of this initiating overpotential is thus of kinetic origin, and it is consequently capable of being reduced through suitable electrocatalysis at the anode.

The possibility of applying anode electrocatalysts of base metal origin is raised. This possibility warrants much further investigation in that the potential for very much cheaper electrocatalysts for the direct methanol fuel cell would reduce substantially the costs of the cell. The ideas have their founding in the Bacon cell which employed fairly passive nickel electrodes. In acidic solution, nickel can be made very passive towards corrosion by suitable reaction with tungsten, and the consequent material is anodically electrocatalytically active towards methanol oxidation. Although the rates of reaction are modest, these materials have not yet been optimised. The incorporation of ruthenium with tungsten in a similar preparation gives negligible catalysis of the methanol reaction, although a modest hydrogen electrode was generated.

The role of tungsten in anode electrocatalysis in acidic electrolytes is raised. Many forms of tungsten have been observed to operate in an electrocatalytic manner with either the methanol or the hydrogen oxidation reactions. Part of this must arise from the high degree of stability of tungsten based materials in acidic solutions; for tungsten carbide this is due to the passivity of the material towards corrosion in strongly acidic electrolytes and its ability to impart passivity to other components such as nickel. Multiple oxidation states of oxidised tungsten, as W(V) and W(VI) and its ability to form the labile hydrogen atom as in HWO_3 may be responsible for this electrocatalytic effect.

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