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Mechanism and electrocatalysis in the direct methanol fuel cell

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Abstract

A unified treatment of the mechanism of electrocatalysis of methanol oxidation on platinum and platinum-containing alloys is put forward. The effect of various alloys is shown to be interpretable within this overall model, and methods for the systematic improvement of the rate of electro-oxidation of methanol are described. Finally, some recent results for model direct methanol fuel cells are given, showing that critical performance parameters for commercial exploitation are now achievable with modern catalytic formulations and cell designs. © 1997 Elsevier Science B.V.

Keywords: Methanol; Electro-oxidation; Fuel cell; Electrocatalysis

1. Introduction

The direct methanol fuel cell (DMFC) is shown schematically in Fig. 1: it consists of an anode at which methanol is electro-oxidised to CO_2 through the reaction

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

and a cathode at which oxygen (usually as air) is reduced to water or steam

$$3/2O_2 + 6e^- + 6H^+ \rightarrow 3H_2O$$

The electrolyte in this cell can be either aqueous acid or alkali, the former being pioneered in the fifties and sixties by Shell and the latter by Exxon–Alsthom. The Exxon programme was abandoned in the late seventies, and the Shell programme in 1981, both decisions being essentially driven by the realisation that oil prices were unlikely to show any substantial rise over the forseeable future, and that commercialisation of the direct methanol fuel cell in traction-based applications would be extremely difficult.

A number of developments have combined to cause a re-appraisal of the DMFC. There is rising concern over the environmental damage caused by the internal combustion engine, coupled with the realisation that the engineering of a truly clean ICE is in itself a major problem, which does not admit of simple end-of-pipe solutions. A comparison of the obvious alternative electrochemical technologies reveals that although batteries offer the prospect of a true zero-emission vehicle, all current batteries have considerable environmental and engineering drawbacks which will be difficult to overcome. On the fuel cell side, the use of a H_2/O_2 fuel cell in traction carries with it severe drawbacks: either the hydrogen must be transported as a gas or in the form of an absorbed phase in a metal alloy, in both cases with considerable resultant weight penalty. If the hydrogen is sourced from a liquid fuel such as methanol moreover, a reformer will be necessary. The disadvantages of reformers are threefold: they add significantly to the overall cost of the cell, they must be operated in a mix of oxygen and water to ensure that the process is exothermic, with consequent

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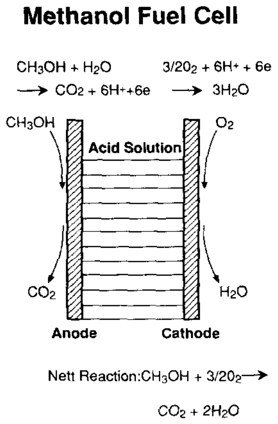

Fig. 1. Schematic of a simple direct methanol fuel cell using a liquid acid electrolyte.

loss of fuel conversion efficiency, and the resultant hydrogen invariably contains CO, requiring the use of less electroactive anodes containing special promoters such as Ru. This type of analysis has led us to the view that the only type of fuel cell likely to be a serious contender for traction is the DMFC, in which the liquid methanol fuel is supplied directly to the anode at which it is electro-oxidised to CO_2. Such a cell also carries with it, at least in principle, the possibility of very rapid response to external demand, as the earlier work that Shell had begun to demonstrate in the late seventies.

The disadvantages of the DMFC are, however, important to rehearse, since the commercialisation of the cell in the medium future depends critically on understanding the limitations of the current science and technology. The primary problem is the low-temperature catalysis required on the anode side. For cells operating with liquid electrolyte at or near 60°C, the overall performance of the anode severely limits the conversion efficiency: large noble-metal loadings are needed, and even under these circumstances, power densities are low. Recently, however, attention has focussed on the adaptation of solid polymer electrolyte technology (SPE) for the DMFC, which has two advantages. The first is that the operating temperature can be raised to 80–100°C; given the relatively high activation energy for methanol electro-oxidation, this increase in temperature offers very real prospects for improved efficiency. The second advantage is by operating with methanol vapour, access to the electrode is improved, and there is, therefore, a considerable increase in current density, even at the same operating temperature as a liquid-electrolyte cell. Primary problems with current SPE technology are the sensitivity of the membrane to water balance, a sensitivity exacerbated by the production of six protons at the anode for every methanol molecule, and the diffusion of unreacted methanol across the membrane, leading to depolarisation of the cathode. Both these problems are currently being targeted, but even with the current far from optimised SPE technology, power densities of approx. $2\,\mathrm{kWm}^{-2}$ have been reported recently by several groups, including Siemens, the Argonne group and the Newcastle group, and these densities make further development of the fuel cell a real commercial possibility.

That said, it is worth emphasising the areas where improvements would be highly advantageous:

1. The activity of the anode must be further improved, either by increasing the operating temperature (currently limited by the properties of the Nafion membrane in SPE cells), or by identifying improved electrocatalysts.
2. The current loadings of noble metal need to be reduced, even though the economic arguments for very low loadings do need to be re-assessed in the light of more realistic views put forward by Stonehart [1].
3. The membrane properties need to be improved both in terms of the water balance sensitivity and by inhibiting the cross-diffusion of methanol.
4. The response of methanol cells to rapid changes in demand needs to be assessed, since the ability to react rapidly will be critical to the success of the cell.

In the remainder of this paper, the main attention will be on the electrocatalysis of methanol oxidation, since this addresses the first two points above. However, as will become evident in the course of this paper, the activity of methanol oxidation catalysts is now relatively high, and although further incremental improvements are likely, it is now possible to envisage power densities of sufficient magnitude to make further technological development worthwhile.

2. The mechanism of methanol electro-oxidation

The basic mechanism for methanol oxidation was reviewed in 1988 [2], and can be summarised in terms of two basic functionalities:

(a) Electrosorption of methanol onto the substrate.

(b) Addition of oxygen to adsorbed carbon-containing intermediates to generate CO_2.

Very few electrode materials are capable of adsorption of methanol; in acid solution only platinum and platinum-based catalysts have been found both to show sensible activity and stability, and almost all mechanistic studies have concentrated on these materials. On platinum itself, adsorption of methanol is now believed to take place through a sequence of steps as:

$$CH_3OH + Pt(s) \rightarrow Pt{-}CH_2OH + H^+ + e^- \quad (1)$$

$$Pt{-}CH_2OH + Pt(s) \rightarrow Pt_2{-}CHOH + H^+ + e^- \quad (2)$$

$$Pt_2CHOH + Pt(s) \rightarrow Pt_3{-}COH + H^+ + e^- \quad (3)$$

$$Pt_3COH \rightarrow Pt{-}CO + 2Pt(s) + H^+ + e^- \quad (4)$$

$$Pt(s) + H_2O \rightarrow Pt{-}OH + H^+ + e^- \quad (5)$$

$$PtOH + Pt{-}CO \rightarrow Pt{-}COOH \quad (6a)$$

or

$$Pt{-}CO + H_2O \rightarrow Pt{-}COOH + H^+ + e^- \quad (6b)$$

$$Pt{-}COOH \rightarrow Pt(s) + CO_2H^+ + e^- \quad (7)$$

Additional reactions that have also been suggested include:

$$Pt{-}CH_2OH \rightarrow Pt(s) + HCHO + H^+ + e^- \quad (8)$$

$$Pt_2CHOH + Pt{-}OH \rightarrow 3Pt(s) + HCOOH + H^+ + e^- \quad (9)$$

or

$$Pt_2CHOH + H_2O \rightarrow 2Pt(s) + HCOOH + 2H^+ + e^- \quad (10)$$

$$Pt_3C{-}OH + Pt - OH \rightarrow 3Pt(s) + Pt{-}COOH + H^+ + e^- \quad (11)$$

or

$$Pt_3C{-}OH + H_2O \rightarrow 2Pt(s) + Pt{-}COOH + 2H^+ + 2e^- \quad (12)$$

Reactions (1)–(4) are electrosorption processes, whereas subsequent reactions involve oxygen transfer or oxidation of surface bonded intermediates.

Considerable controversy surrounds the relative rates of the above processes and the identity of the dominant species on the surface, but the following are the key experimental observations for platinum in the bulk form:

1. Electrosorption of methanol is slow on bulk platinum at lower potentials, and shows an activation energy of 35 kJ mol^{-1} [3].
2. The dominant adsorbed species in the lower potential region is linearly bonded CO at higher concentrations of methanol. At lower methanol concentrations, $Pt_3C{-}OH$ is favoured [5,6]. Bridged forms of adsorbed CO have also been detected, and it appears that the energy differences between the various forms of linearly bonded and doubly and triply bridged CO species are small [8].
3. Kinetic isotope studies on methanol oxidation favour reaction (6b) rather than (6a), with the water molecules co-adsorbed on the platinum [4].
4. At potentials above approx. 0.5 V vs. NHE, there is a steady loss of adsorbed CO from the surface of the platinum and a gain of CO_2. Above 0.7 V, the surface is almost free of CO_{ads} [3,7].
5. Isotope measurements for methanol oxidation below 0.5 V show that neither ^{13}CO nor $^{13}C{-}OH$ formed on the surface from electrosorption of $^{13}CH_3OH$ exchange on immersion in $^{12}CH_3OH$, not even during oxidation of the $^{12}CH_3OH$ to $^{12}CO_2$ [9,10].
6. Adsorption of CO onto platinum from solution appears to take place with the formation of islands of adsorbate [11]; electroactivity appears to be restricted to the outsides of these islands.
7. For CO adsorbed at the metal–gas interface, it is known that the adsorbed species are highly mobile [12], with the mobility being facilitated probably through multiply bonded CO moieties, consistent with the apparent small energy differences between these different forms as discussed above.
8. Morphology appears to play a major role in the electroactivity of platinum [13], with roughened platinum showing much higher activity [14]. This increase in activity has been associated with: (i) a decrease in the strong specific adsorption of HSO_4^-

on large planar areas of the platinum (this adlayer is strongly stabilised by hydrogen bonding on ordered interfaces [16] and is known to inhibit methanol adsorption [15,32]); (ii) the increased formation of extended step sites that have been associated with the primary methanol adsorption process [17]; (iii) the formation of isolated low-coordinate platinum ad-atoms, which is known to take place during roughening [18], and it has been suggested that such platinum atoms may be much more easily oxidised, as evidenced by XPS, giving rise to Pt–O species at potentials far below that at which planar platinum is oxidised [19].

9. Methanol adsorption is inhibited quite generally by adsorption of anions: chloride ions strongly inhibit methanol oxidation at platinum [20], and bromide and iodide entirely arrest the process. Of the oxy-anions, perchlorate appears least to affect the oxidation rate of methanol [21], but unfortunately, platinum appears to catalyse the reduction of perchlorate to chloride [22], which even in small quantities is sufficient to poison the electrode. Adsorbed phosphate also inhibits the rate of methanol oxidation, presumably through competitive adsorption [23].
10. Studies of methanol adsorption and oxidation on single-crystal surfaces of platinum shows considerable sensitivity to the Miller indices of these surfaces. The adsorption of methanol to form linearly bonded CO is most extensive on Pt(100) and those surfaces having (100) terraces; on the Pt(211) surface, substantial multi-bonded adsorbate is present, and in sulphuric acid electrolyte, this is also true of Pt(111) and Pt(110) [15,24]. Time-resolved studies have shown that on Pt(100), initial adsorption of methanol takes place to give multiply bonded CO_{ads} species, which only convert to linearly bonded species such as –C≡O or (possibly) –CHO at longer times [25]. The rate of oxidation of methanol is highest on the Pt(110) surface [15,32], with instantaneous potential-step measurements giving currents as high as 156 mA cm^{-2} for the initial chemisorption process. This process on Pt(1 1 0) has the initial step (1 above) as rate limiting until the surface CO coverage attains a stationary value. An important caveat on all single-crystal data is the increasing realisation with the advent of in situ scanning-probe methods that surfaces undergo significant reconstruction in solution, reconstruction that may be driven by the adsorbate itself (see discussion in Ref. [1]).
11. Studies of the electrochemical kinetics is bedevilled with difficulties over surface pre-treatment and control of the coverage of intermediates. Bagotzky and Vasil'ev [27], who used pulse methods to determine the coverage of chemisorbed intermediates, and attempted to derive functional expressions connecting current, coverage by intermediate (θ) and potential: the final expression has the form $j\sim\exp(\beta f\theta)\exp(\beta'\mathbf{F}E/RT)\cdot[H^+]^{-1}$, where **F** is the Faraday constant (96 500 C mol^{-1}), β=0.4–0.5, f=10–11 and β'=0.78–0.86, suggesting that the coverage of adsorbed CO is governed by a Temkin-type adsorption isotherm. This expression is consistent with a mechanism in which there is an attack on adsorbed CO by water in the double layer in the rate-limiting process. Other later studies [27,28] showed different behaviour; in particular, Inada et al. [28] found a current at long times of the form $j\sim\exp(-k\theta)\exp(0.56\,E\mathbf{F}/RT)$ for $E<0.55$ V, consistent with adsorption being rate limiting, whereas Arimata et al. [29] suggested that the rate-limiting step was probably oxidation of the Pt–CH_2OH intermediate by Pt–OH. Christensen et al. [13] measured the rate of formation of CO_2 rather than the current, to avoid any complications due to parallel reactions, and simultaneously

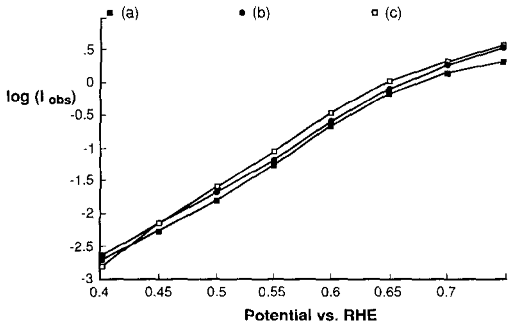

Fig. 2. Measured Tafel slope for CO_2 generation at a platinum electrode from in situ FTIR data. The platinum electrode was cycled initially in pure 1 M H_2SO_4 and then held at 0.05 V vs. RHE for approx. 1 h before the addition of methanol to the concentrations shown. The potential was then stepped up in 50 mV steps, and the rate of evolution of CO_2 measured at each potential.

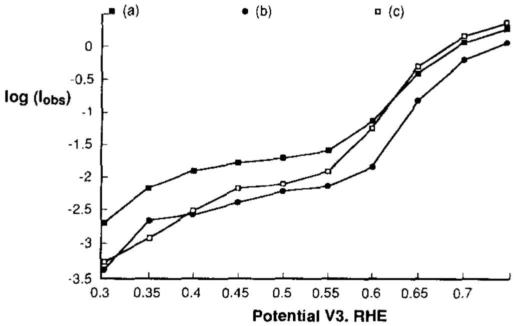

Fig. 3. Similar to Fig. 2 save that the platinum electrode was initially cycled in the acidifed methanol solution before being held at 0.05 V vs. RHE and then stepped to higher potentials.

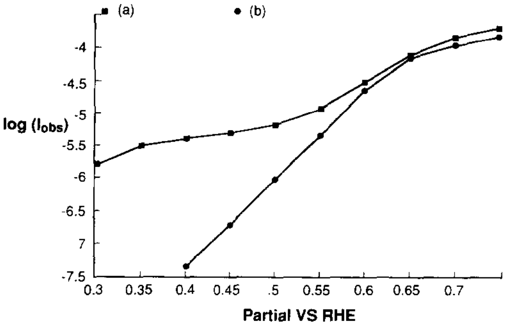

Fig. 4. The dependence of CO_2 generation rate vs. potential for measurements carried out as in Fig. 2. The difference between (a) and (b) is that in experiment (b) the electrode was held at 0.05 V for ca. 1 h whereas for (a) measurements were started without any delay, with the result that the surface relaxation so evident in (b) could not take place.

monitored the coverage spectroelectrochemically. They obtain a similar Tafel slope to that reported by Bagotzky and Vasil'ev [27] for an equilibrated platinum surface, as shown in Fig. 2, but were able to show that for roughened platinum, the Tafel slope became large, as shown in Fig. 3, suggesting that a chemical process was limiting the rate on this type of surface; this chemical process was identified tentatively as CO migration from CO_{ads} islands to active sites, a result supported by activation energy measurements [73].

3. Summary of mechanistic conclusions for platinum

Although there remain areas of controversy over the details of the methanol oxidation process, which are certainly connected with the existence of multiple pathways with similar activation energies on the platinum surface, there is little doubt that the primary processes can be represented as follows:

1. Adsorption of methanol, most easily at energetically favoured sites such as steps.
2. Sequential proton stripping from the methanol to give a series of multiply bonded intermediates that eventually convert to linearly bonded CO; evidence for the short-lived hydrogenated intermediates on platinum arises from IR [6], DEMS [5], time-resolved [25] and product studies [26].
3. Kinetic analyses suggest that there are two extreme types of mechanism for methanol oxidation on platinum: one involves attack of water on CO molecules on the outside of the chemisorbed CO islands in a type of Reppe process, and the second involves rate-limiting migration of CO from the edges of the islands to active sites, perhaps Pt–O as identified by XPS. Currents are always higher on roughened platinum than on equilibrated platinum, at least for potentials below about 0.55–0.6 V, as seen in Fig. 4; above this potential, CO_{ads} is oxidised rapidly from the platinum surface, and FTIR data [30] suggest that intermediates such as Pt_3COH may be oxidised directly to CO_2 at higher potentials. This change of mechanism at higher potentials has also been detected by spin-trap epr data [31], which again detects formyl radicals.

3.1. *Methanol oxidation on platinum particles*

Although the oxidation of methanol on platinum particles is far more important technologically than bulk platinum, the number of mechanistic studies has been very much smaller. The following studies are of key importance:

1. There is considerable controversy over whether there exists a "size effect" in methanol oxidation. Earlier data from Shell [33] suggested that there was a pronounced size effect, with an optimal Pt cluster diameter of ca. 3 nm, and the Oxford group

suggested that an optimum diameter of ca. 2 nm was found in their own work [19]. The existence of an optimum size would undoubtedly be expected from the structure-demanding nature of the adsorption process, with the multiply-bonded intermediates postulated above. However, Watanabe et al. [34] do not find any evidence for size effects, even for particles as small as 1.4 nm, and have suggested that earlier work may have been flawed by failure to control the interparticle distance.

2. In situ IR studies of particles have suggested that there is a decrease in linearly bonded CO, with an increase in the bridged form at higher overall coverage [35]. A more recent study by Christensen et al. [36] has clarified the situation: chemisorption of methanol on Pt particles has been found to be far faster at lower potentials than on bulk platinum, strongly suggesting that methanol chemisorption takes place through step or other crystallographic defect sites. By following the subsequent evolution of the CO FTIR signal with potential, shown in Fig. 5, these authors were able to establish that: (i) methanol initially adsorbed at the step sites before further being oxidised and transferred as CO_{ads} to the particle terraces, methanol remaining at the step sites was, however, only partially dehydrogenated; (ii) the partially oxidised step-site-bound intermediate was easily oxidised to formic acid at low potentials, a result confirmed by DEMS; (iii) some CO_{ads} could then migrate from the terraces to the step sites; (iv) the remaining CO_{ads} on the terraces could then transform into bridged forms; (v) oxidation of the adsorbed CO then took place through an active-site mechanism as for bulk platinum. This mechanism clearly implies that Pt particle activity will be a sensitive function of morphology, and will depend, for example, both on the reduction method and on the nature of the underlying carbon, as has been observed [19,37].

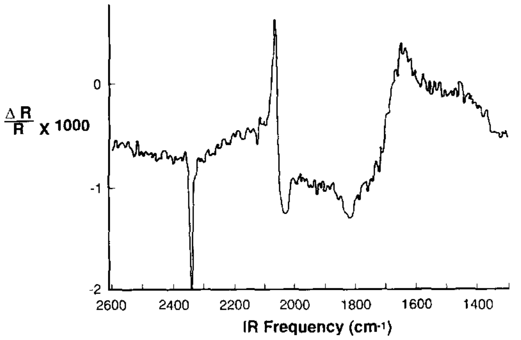

Fig. 5. In situ FTIR difference spectrum collected at 400 mV vs. RHE during an experiment in which the potential of the platinum particle electrode (immersed in 1 M H_2SO_4/1 M CH_3OH) was increased from 0.05 V vs. RHE in 50 mV steps. The spectrum (8 cm^{-1} resolution, 100 co-added averaged scans requiring ca. 60 scans s^{-1}) was normalised to the reference spectrum taken at the base potential of 0.05 V. The band at 2342 cm^{-1} is assigned to CO_2, the 2065–2030 cm^{-1} "bipolar" band to singly bonded CO, the 1820 cm^{-1} band to triply bonded CO, and the loss at 1640 cm^{-1} and the gain from 1680 cm^{-1} to ca. 2000 cm^{-1} to water associating with the protons produced during electro-oxidation of the methanol.

4. Platinum promotion

Platinum itself, though widely studied as an electrocatalyst for methanol oxidation, is not sufficiently active to be useful commercially, and there has been an intensive search for other active materials. This search has been illuminated by the mechanistic analysis given above; in particular, the bi-functionality has led to the search for materials that might be able to combine with platinum, with the latter acting to chemisorb methanol and the promoter then providing oxygen in some "active" form to facilitate oxidation of the chemisorbed CO.

1. The simplest method for enhancing oxidative activity is to generate more Pt–O species on the platinum surface by incorporation of metals as alloys that then dissolve to leave highly reticulated and active surfaces. Alloys such as Pt_3Cr and Pt_3Fe have been shown to be more active than platinum by virtue of this process, as shown in Fig. 6(left) and (right), and the same may be true in part for Pt_3Sn, though there is controversy here. The drawback with this method of promotion is the poor long-term stability of the particles. In addition, improved methods for platinum particle deposition are important in creating improved surface area and surface morphology. The use of more powerful reducing agents can improve performance, as shown in Fig. 7, and by the use of controlled colloid deposition through the

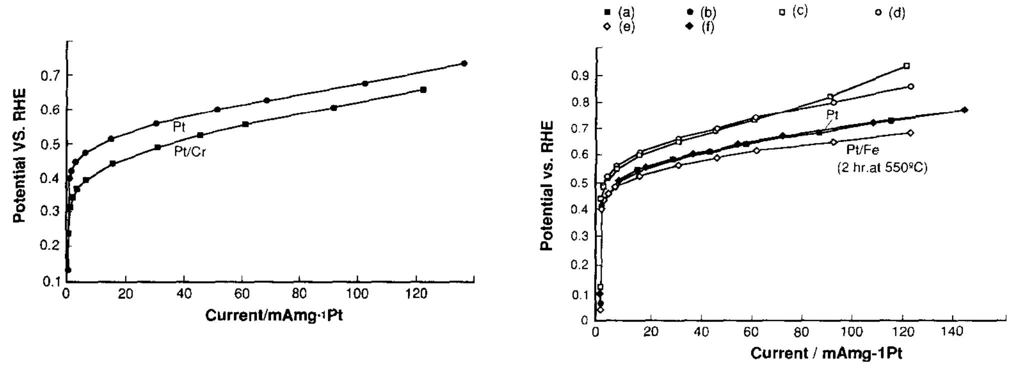

Fig. 6. (Left) Polarisation curves obtained for (a) platinum and (b) platinum/chromium particulate catalysts dispersed on carbon (XC-72) at 60°C in 2.5 M H_2SO_4/1 M CH_3OH. The current is plotted at mA mg^{-1} Pt catalyst to ensure that the data are comparable. (right) Polarisation curves for (a) platinum, (b)–(f) platinum/iron particulate catalysts under the same conditions as in the left panel. The main difference between the catalysts lies in the temperature at which they are heat treated during preparation: (b) Fe adsorbed on platinum without heat treatment; (c) 1 h at 700°C; (d) 1 h at 600°C; (e) 2 h at 550°C; and (f) 3 h at 500°C.

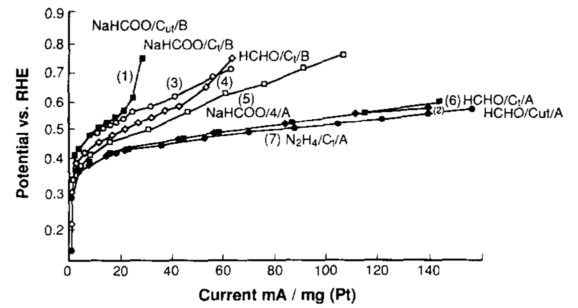

Fig. 7. Effect of reduction procedure on the activity of platinum particulate catalysts for methanol oxidation. The polarisation curves were all obtained at 60°C in 2.5 M H_2SO_4/1 M CH_3OH and the catalysts were prepared by reduction of chloroplatinic acid. Details of the preparation procedures are given elsewhere [37] in brief, electrodes were fabricated from untreated carbon XC-72 (C_{ut}) or from XC-72 treated for 1 h under flowing CO_2 giving a 27% weight loss (C_t) and with either direct reduction of the chloroplatinic acid in situ onto the carbon (Method A) or by first impregnating the carbon with the chloroplatinic acid, drying in air at 110°C for 12 h and then reducing (Method B). The reducing agents used were NaHCOO, HCHO and N_2H_4 and the electrodes investigated are: (1) NaHCOO/C_{ut}/B; (2) HCHO/C_{ut}/A; (3) NaHCOO/C_t/B; (4) HCHO/C_t/B; (5) NaHCOO/C_t/A; (6) HCHO/C_t/A; (7) N_2H_4/C_t/A.

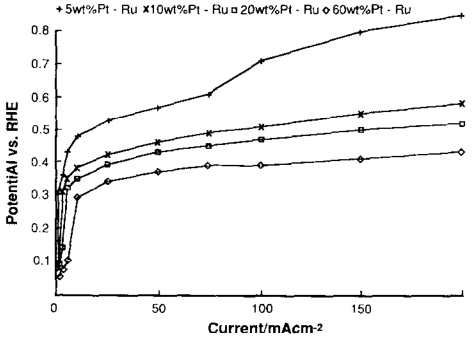

Fig. 8. Polarisation data for Pt/Ru electrodes in 2.5 M H_2SO_4/1 M CH_3OH at 60°C with increased catalyst loadings made by the "sulphito" route, in which a collidal hydrous PtO/RuO_2 sol is prepared directly from a $[H_3Pt(SO_3)_4]^{3-}/[Ru(SO_3)_3]^{4-}$ solution by oxidation with H_2O_2 in the presence of carbon, which is impregnated by the sol in situ. The dried catalysed carbon is then reduced by H_2 to form 2 nm diameter regularly dispersed Pt/Ru particles.

"sulphito"-route, extremely high activities can be found at higher loadings, Fig. 8.

2. A second approach has been the use of surface ad-atoms, deposited by upd on the platinum surface. These have been studied extensively [1,38,39], with Au [40] being identified early on, but with most recent attention being on Sn [41–43] and Bi [43]. Several modes of operation have been suggested for these ad-atoms, including the blocking of hydrogen adsorption, the ability to modify the electronic properties of the platinum, the ability to act as redox centres, the blocking of poison adsorption sites or the ability of the ad-atom to induce Pt–O formation on neighbouring sites, creating additional active sites for oxidation of CO_{ads}. The ability of both Sn and Bi ad-atoms to enhance the rate of methanol oxidation has been queried

in a recent paper [43]; the authors found that under very carefully controlled conditions, the adsorption of these metals actually inhibited methanol oxidation, even though there is good evidence that Bi adsorption also inhibited formation of adsorbed CO [44].

3. A third type of promotion is the use of alloys of platinum with different metals, where the second metal forms a surface oxide in the potential range for methanol oxidation. This is the basis for studies of Pt–Sn, Pt–Ru, Pt–Os, Pt–Ir, etc. Unlike the Sn-ad-atom data of [43], there seems little doubt that Pt_3Sn as an alloy does show catalytic behaviour [41,45–47] though this may simply derive from the same mechanism as Pt_3Cr, perhaps with the resulting fractal particle surface being stabilised by tin adsorption. Studies of Pt alloyed with the other noble metals has shown that Ru has by far the largest effect, giving a real catalytic advantage, as shown in Fig. 9 [41,48]. We return to the possible mechanisms of this effect below. Ir and Os were also found to act as promoters in this study [48], with Au and Pd inhibiting the reaction. Pd was also not found helpful in acid solutions in earlier studies [49]. Amongst the non-noble metals, electrodeposited Pt–Re alloys were reported to show substantial enhancement by Cathro [50], a result that seems not to have been followed up. Reports of very strong enhancement for electrodeposited Mo on Pt have also been reported [51,52], particularly at low currents, where there seems to be a different oxidation mechanism operating. Given the effectiveness of binary alloy formation, particularly with Ru/Pt, attention has turned recently to ternary alloys. The apparently different promotion mechanisms for Pt/Sn and Pt/Ru led Troughton and Hamnett [47] to explore the Pt/Ru/Sn system, but it was found that alloying Pt/Ru with tin tends to expel the Ru, leading to no advantage. Of other ternary alloys studied, only Pt/Ru/Ga showed any unequivocal advantage, and this was slight (Fig. 10) [53].

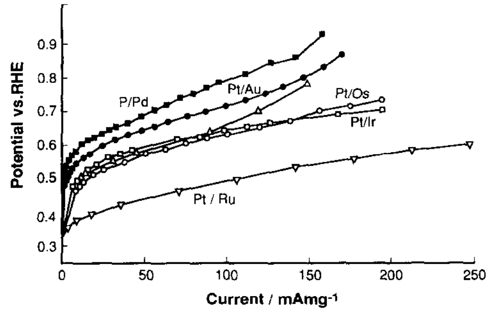

Fig. 9. Polarisation data for Pt/M alloys measured under the same conditions as Fig. 7. Details of the fabrication methods can be found in Ref. [48].

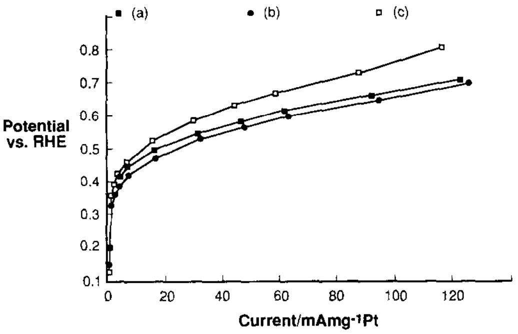

Fig. 10. Comparative polarisation data for: (a) Pt–Ru; (b) Pt–Ru–Ga; and (c) Pt–Ru–Cr electrodes measured under the same conditions as Fig. 7. The details of electrode manufacture are given in Ref. [53].

4. The fourth type of promoter to be described in the literature is a combination of Pt with a base-metal oxide. Initially, these were reported by Hamnett et al. [54], with Nb, Zr and Ta being found most active for Pt promotion, particularly at higher currents, as shown in Fig. 11(a) and (b). However, although the effect on Pt itself is clear, attempts to use ZrO_2 to promote Pt/Ru were unsuccessful [55], suggesting that the original mechanism for promotion by these oxides is similar to that for Ru itself [56]. Hamnett et al. [54] originally identified WO_3 as an inhibitor, but more recently, Shen and Tseung [57,58] have identified hydrous WO_{3-x} as a substantial promoter for activity when Pt is electrodeposited on its surface, and this was confirmed separately by Shukla et al. [59] who reductively co-deposited Pt and WO_{3-x} onto a porous carbon substrate. Related catalysts are formed by doping tungsten bronzes, of the structure $Ln_{0.1}WO_3$, with Pt; in these catalysts, as in the ones reported by Tseung, the W seems to be providing a redox couple, cycling between W(IV) or W(V) and W(VI). Interestingly, the enthalpy of activation is

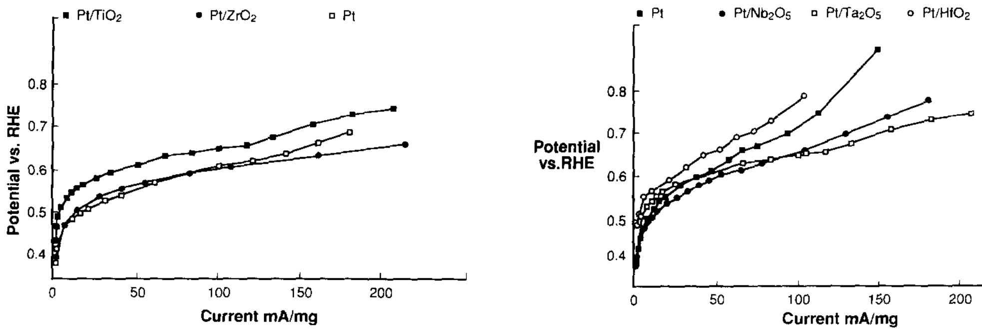

Fig. 11. (a) Comparative polarisation data for Pt; Pt/TiO_2 and Pt/ZrO_2 measured under the same conditions as Fig. 7. (b) Idem for Pt; Pt/HfO_2; Pt/Nb_2O_5 and Pt/Ta_2O_5. All electrodes were fabricated as described in Ref. [54].

much lower for these catalysts than for Pt itself [60]. There have also been reports of Pt on mixed In/Pb oxides on carbon, which showed activity but poor stability [61].

5. In addition to the electrodeposition or reductive deposition of Pt onto an oxide surface, it is possible to incorporate the Pt directly into many oxide structures, and these species have been examined recently. Perovskite-based oxides, in particular, $SrRu_{0.5}Pt_{0.5}O_3$, were found to give good current densities when used as electrodes in Nafion-based cells [62], and similar results were reported for $Dy_xPt_3O_4$ [63]. It is unclear how stable these oxides are in the longer term in acidic environments, and reductive decomposition through methanol adsorption to give finely divided platinum particles at the surface which act as the main catalytic sites, remains a plausible mechanism.
6. Although platinum is overwhelmingly the most active catalyst for electro-oxidation of methanol, the high loadings necessary for commercial performance have fuelled the search for other materials. There are other noble-metal catalysts, such as Ir, that have been investigated [64,65], but they are all less active than Pt and offer little in the way of economic advantage. It now seems to be the case that WC shows some activity for methanol oxidation, particularly if the material is annealed with carbon in a He atmosphere, though the activity remains far below Pt [66]. Some amorphous metal alloys are active, the most stable in acid being apparently NiZr [67,68], which forms a thick passivating oxyhydroxide film on which the electro-oxidation of methanol can take place. Hays et al. [68] suggest that the mechanism of this reaction must involve Ni^{3+} ions but were unable to devise a persuasive reaction route. Interestingly, alloys such as NiZr and NiTi with a few % platinum are extremely active for methanol oxidation by comparison [69], and there are real worries about the possibility of Pt contamination in this work.

5. Mechanism for promotion of platinum by ruthenium

Considerable effort has been expended to clarify the nature of ruthenium promotion on platinum, since the better understanding of this process might allow us to design improved catalysts.

1. The alloying of ruthenium and platinum has been postulated to give rise to an electronic effect in which electrons are transferred from Ru to Pt [2]. However, the suggested direction of electron donation has been challenged recently, particularly from FTIR studies on well-defined bulk alloy [70] and on Pt–Ru particles [71], both of which show a reduction in the coverage of the electrode by CO_{ads} at any given potential, and an increase in the absorption frequency of the bound CO. This latter effect must be electronic in origin, and is consistent with CO being less strongly adsorbed through a reduction in the back π-bonding from Pt to the CO π^* orbital. The reduction in π back-bonding will also lead to a higher positive charge on the carbon atom, rendering it more liable to nucleophilic attack by water, and permitting

oxidation of CO at lower potentials. This effect has been verified by DEMS studies [72], which also demonstrated that methanol chemisorption does not take place at pure Ru at room temperature, though CO is oxidised at Ru at potentials 200 mV more negative than Pt alone; formation of a Pt–Ru alloy shifts the CO oxidation maximum in cyclic voltammetry to even more negative potentials, again suggesting an electronic effect.

2. A second major effect of ruthenium is to increase the coverage of Pt–Ru surfaces by oxy-species. An XPS study [19] showed that the presence of Ru significantly enhanced the amount of Pt–O species present, a result confirmed by later work [75–77]. Moessbauer data by the same authors [78] demonstrated that in co-deposited Pt–Ru particulate electrodes, the Ru was present in the form of an oxyhydroxide, rather than a well-defined RuO_2 surface phase, and the slow failure of catalysts made in this way was attributed to transformation of the hydrous oxide to the more inactive anhydrous phase [79].
3. Studies on well-defined alloy surfaces, with known surface compositions [73,74] have shown that low Ru coverages lead to facile chemisorption of methanol but, as expected, to rate-limiting oxidation of CO_{ads}, with the rds being CO migration to active Ru clusters. As indicated above, Ru itself has always been found to be inactive for methanol oxidation at room temperature, and it has been something of a puzzle that practical Pt–Ru electrodes are optimised at about 50% a/o for each component. This puzzle has now been resolved with the observation that Ru has a high activation energy for methanol chemisorption, but that at >60°C, methanol can adsorb both on platinum and ruthenium [73], and the reduction that is found in adsorption rate at room temperature for Pt–Ru alloys as compared to pure Pt is not found at 60°C save at very low methanol concentrations.

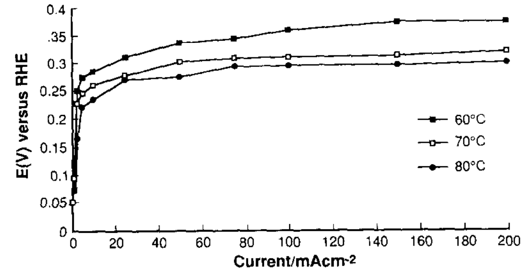

Fig. 12. Ultra-thin electrode fabricated from carbon/Nafion mixture reverse fed by a 50 : 50 mixture of CH_3OH : water and having Pt–Ru catalyst deposited by the "sulphito" route to 40 wt% Pt–Ru, with a loading of 2 mg cm^{-2}. The electrode is fabricated by hot pressing the Nafion/carbon mix onto a Nafion membrane [81], and the three polsarisation curves were obtained at 60–80°C in a half cell using a 2.5 M H_2SO_4 as the electrolyte in contact with the Nafion membrane of the electrode.

6. Limit in activity of Pt–Ru electrodes and the current performance figures

A key concern in the development of the DMFC is the question of whether Pt–Ru electrodes are capable of further improvement and development or whether there is a natural limit. For methanol electro-oxidation at 60°C in 2.5–3 M H_2SO_4/1 M CH_3OH on Pt–Ru at 0.4 V, rates close to 40 μA cm^{-2} have been quoted for real surface area, and for lower concentrations of acid, where there is less competitive anion adsorption, values near 160 μA cm^{-2} are suggested [73,80] at the same temperature. Given an activation energy for Pt–Ru of 60 kJ mol^{-1}, this would correspond to approx. 200 mA cm^{-2} for a loading of 1 mg cm^{-2} at 60°C, and would increase by a factor of 3.5 at 80°C and by a factor of 10 at 100°C.

That these figures are conservative is shown by recent studies in Newcastle [81]; Fig. 12 shows anodes with a loading of 2 mg cm^{-2} and a performance of better than 200 mA cm^{-2} at 0.3 V vs. NHE at 90°C. The Newcastle group have also fabricated SPE cells giving a performance of 0.47 V at 200 mA cm^{-2}, and an optimum power density of 1.6 kW m^{-2} [81], and more recent work with pressurised systems has shown power densities of 3.5 kW m^{-2} in oxygen (Fig. 13) and, very encouragingly, 2 kW m^{-2} in air (Fig. 14) [82]. Interestingly, the Newcastle cells are stable with time, at least over a period of days, suggesting that the methods now used for fabricating such electrodes have succeeded in ameliorating, at least to some extent, the problems of oxide dehydration that plagued earlier catalyst formulations.

The fact that the cell and anode performance even exceeds that predicted from intrinsic activity figures

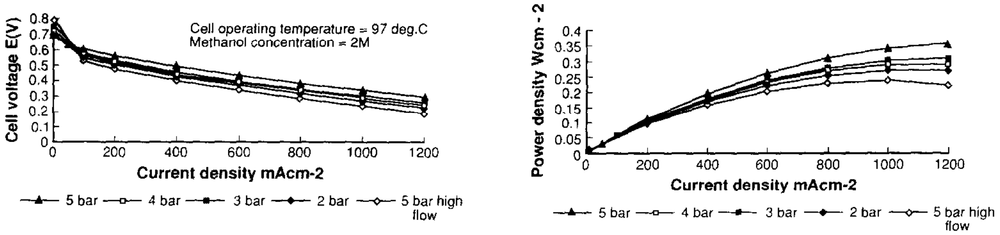

Fig. 13. Performance figures for a complete prototype DMFC (9 cm^2) with vapour feed methanol/steam at ca. 100°C. The cell is fabricated by hot pressing Nafion-bound catalysed carbon electrodes onto both sides of a Nafion membrane and mounting between carbon cloth current carriers. The cell operating temperature is 95–100°C and the effect of the pressure of oxygen shown. Note the very high current densities and resultant power densities.

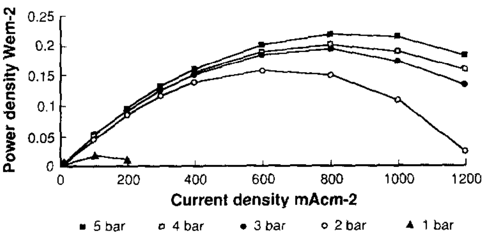

Fig. 14. Performance figures for the same cell as in Fig. 13 but with air rather than oxygen feed on the cathode.

[73,80] has been due in part to the successful realisation of SPE-based DMFC's, for which it is clear that activity is high, and methanol cross-over not as serious as was first thought, particularly when operating under pressurised conditions. Even operating at 80°C, these cells are capable of generating commercially interesting power densities with Pt–Ru anodes. In addition, improved methods of depositing Pt–Ru have led to far better control over the particle size and surface area, with the result that much of the electrocatalytic work reported above has been overtaken simply by better electrode and catalyst fabrication processes for Pt–Ru, though it is also true to say that much of the thrust of this improvement stems from the increased insights into the mechanism of electrocatalysis.

7. Summary

1. The current densities achievable in principle on Pt–Ru are now starting to be approached experimentally. Such current densities are sufficient for fuel cells operating above 2 kW m^{-2}.
2. The most urgent task to be faced in further development of the DMFC is probably not the identification of new electrocatalysts, but rather the improvement in the membrane properties needed to prevent depolarisation of the cathode and dehydration effects at and near the anode.
3. A second task that needs to be carried out is the investigation of the speed of response of a simple fuel cell to changing demand. The thermal fluxes in such cells have not been explored, but are likely to be considerable, and the stability of the membrane to such fluxes also need to be established.
4. In terms of supporting work, it would be highly desirable to pin down unequivocally the mechanism of ruthenium promotion, in order that further improvements in catalyst design can be carried out. The possibility of discovering a wholly novel catalyst for methanol oxidation cannot be assessed in any rational way, but the probability of incrementally improving the activity of current catalysts by establishing the mechanism whereby they operate is very high.

The DMFC has reached an important watershed in its development. It is likely that working stacks will be constructed within the next few years, and the research impetus is gathering pace very quickly, bringing new challenges for the engineer as well as new demands on the electrochemist. This development represents a remarkable achievement in combining catalytic insight and practical electrode manufacture; the fruits of this combined scientific and engineering programme may well revolutionise the way in which we power our cars.

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