

THE METHANOL-AIR FUEL CELL: A SELECTIVE REVIEW OF METHANOL OXIDATION MECHANISMS AT PLATINUM ELECTRODES IN ACID ELECTROLYTES

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Summary

Over the past few years there has been a resurgence of interest in methanol oxidation in acid electrolytes, where platinum group metals are the only practical catalysts. The recent literature concerning the adsorption and oxidation processes occurring at platinum in acid solutions is reviewed. The overall model based on contemporary data assumes that methanol adsorption follows Langmuir kinetics at low surface coverages and Elovich kinetics at higher values. The 'poisoning' intermediate (probably COH) is susceptible to an ageing process, rendering it less active, and its ultimate removal is achieved via a chemical reaction with an electroadsorbed water molecule.

Bimetallic catalysts which adsorb both water and methanol at low potentials are much more active than platinum alone. Modern, highly-dispersed catalysts on carbon supports have been reported with high specific activities. However, for commercial viability (particularly with regard to automotive applications) considerable improvements are still required.

Introduction

Since the concept of a fuel cell was first proposed early in the nineteenth century [1] and its feasibility subsequently proven by Grove [2], research into this topic has enjoyed several waves of popularity. However, the fundamental electrocatalytic problems associated with the anode and cathode reactions have meant that such devices have been economically viable in very few applications.

A considerable research effort has been stimulated by the possibility of producing an efficient and relatively cheap power source requiring very little maintenance. The fuel cell also has a high energy density, consumes conven-

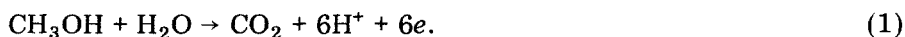
tional fuels and air, operates quietly, and produces less obnoxious by-products than the internal combustion engine.

In the U.S.A. particularly, much work has been concentrated on the development of indirect (*i.e.*, hydrogen produced by cracking methanol) hydrogen-air fuel cells for stationary power generation. This programme is sponsored largely by the U.S. Department of Energy and the Electric Power Research Institute. A number of fuel cells have been constructed operating over a wide range of temperatures. The drawbacks of low temperature cells (working below 200 °C) are mainly connected with the low reaction rates, *i.e.*, inefficient electrocatalysis. This is not so critical at higher temperatures but other problems such as corrosion and electrolyte conductivity emerge.

The type of fuel consumed is also an important factor to be considered. Gaseous fuels demand porous electrodes designed to enable the electrochemical reaction to occur at the gas-liquid-solid interface. Liquid fuels are preferable in that a simpler electrode construction is required and also storage and handling are easier.

Studies of the anodic activity of water-soluble organic compounds at platinum electrodes have shown that the primary alcohols are generally the most reactive [3] (though considerably less reactive than hydrogen), and that their reactivities are generally lower in acid than in alkaline electrolytes [4].

Methanol is a particularly promising compound for use in a low temperature, aqueous electrolyte fuel cell, yielding six electrons per molecule in acid solution:



Acid electrolytes are preferable when carbonaceous fuels are to be employed in order to avoid the precipitation of carbonate in the electrolyte and the consequent harmful effects on the electrodes. Alkaline electrolytes which may be gradually converted to carbonate by reaction with CO₂ will suffer from increasing concentration polarisation at the electrode surface and decreasing conductivity of the electrolyte.

The major problem in the development of direct methanol-air, acid electrolyte fuel cells is electrocatalytic in nature. The fuel reaction requires the use of noble metal catalysts (and in particular platinum) in substantial amounts (several milligrammes per square centimetre of electrode area). Whilst some enhancement in performance can be made *via* engineering developments, such improvements are small in relation to that required in order to attain commercial viability. It is therefore the purpose of this paper to review recent investigations of the adsorption and oxidation processes of methanol at platinum electrodes in acid electrolyte solutions.

Initially, in acid solution, smooth Pt produces a very high catalytic activity [5, 6], but this rapidly decreases due to the poisoning resultant from partial dehydrogenation of the methanol molecule.

Biegler and Koch [5] have shown that the initial current density is about 10⁴ - 10⁵ times higher than the quasi-steady state current density (*i.e.*,

the value attained after a few minutes on load). This has been confirmed by Andrew and McNicol [6], and Fig. 1 shows a typical current-time transient in the potential range 0 - 0.5 V vs. N.H.E. A dramatic fall in current is observed over the first half second. The problem is clearly that the dehydrogenated methanolic residue builds up on the catalyst surface blocking Pt sites and thus inhibiting further reaction of methanol. Considerable effort has been expended in attempting to establish the identity of the residue and also to determine the agent or agents responsible for its ultimate removal.

Adsorption kinetics

Much of the earlier work on methanol oxidation has been reviewed [7 - 15] but only general conclusions can be drawn from the great volumes of conflicting data published. An attempt to reconcile the differences in reported methanol adsorption data has been made by Kazarinov *et al.* [16]. Here, the authors compared information obtained by electrochemical and radiotracer techniques on the adsorption kinetics of methanol. The radiochemical work of other groups [17, 18] was reproduced qualitatively and the electrochemical work of others confirmed quantitatively [19 - 23]. It was concluded that differences between the electrochemical and radiochemical data could be explained by assuming that the impurities present in labelled methanol solutions were the products of autoradiolysis, so that their nature did not depend on the technology and specific features of preparation of labelled methanol samples. The quantitative differences in the data obtained by different authors with labelled methanol were explained by different impurity contents which, in particular, would depend on time and storage conditions of the radioactive preparations.

Following a critical assessment of previous findings [20, 24], Biegler [5, 25] was able to show that the adsorption of methanol was potential

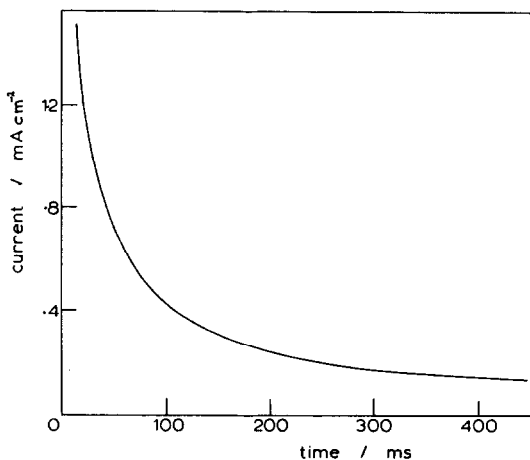


Fig. 1. Current-time profile for methanol on platinum foil at 60 °C.

independent between 0.2 and 0.5 V. Kazarinov *et al.* [26] and the Polish school [27] were able to confirm this, the latter having earlier observed [18ii] a region of potential independence between 0.4 and 0.55 V. No simple correlation between radiochemical and electrochemical methods could be found and it was concluded that Elovich kinetics [28]

$$\theta = a + \frac{RT}{\alpha F} \log t \quad (2)$$

(where θ represents surface coverage and t corresponds to time) are obeyed for high surface coverages, but that the region of applicability of Langmuir kinetics

$$\theta = 1 - \exp(-kt) \quad (3)$$

is wide. The radiochemical results could be compared with those of Breiter [8] yielding an electrons-per-molecule figure of approximately 2. The species $\text{H}_2\text{C}_2\text{O}_3$, which is equivalent to the simultaneous adsorption of HCO and COOH in equal amounts, has been proposed as a chemisorption product [8]. The discrepancies between this and electrochemical data still leave the nature of the adsorption product open to question. That Langmuir kinetics should be obeyed in the double layer region is in marked contrast with the data of Bagotsky and Vasiliev [19], Biegler and Koch [5], and Kazarinov *et al.* [26, 29] which support Elovich [28] conditions. However, for the case of formic acid, the data reported by Brummer and Makrides [30] and Capon and Parsons [31] also provide evidence for the Langmuir model of adsorption.

The adsorption of methanol exhibits many similarities to the processes occurring in formic acid solutions and frequent comparisons have been made. Capon and Parsons [32] summarise the most important features recognised up to 1972 as follows:

(a) The strongly adsorbed species formed on a Pt electrode from HCOOH and from CH_3OH are the same.

(b) The strongly adsorbed intermediate acts as an inhibitor to the overall reaction.

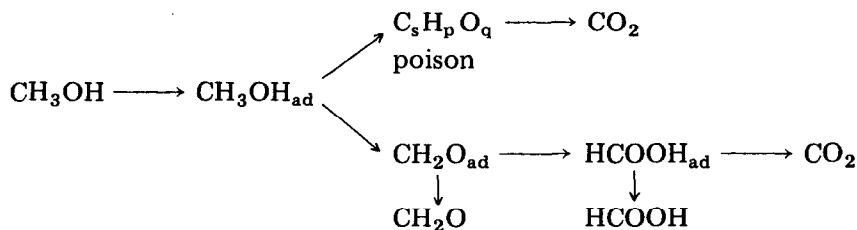
(c) The chemical formula of the intermediate is most likely to be $\frac{x}{x}\text{COH}$ or $x\text{COOH}$, or a mixture of the two, with the majority of opinion favouring a higher proportion of $\frac{x}{x}\text{COH}$.

(d) The intermediate is of constant composition from zero to 0.6 V.

Belanger [32a] has shown that marked inhibiting effects can be observed in the presence of low concentrations of anions (10^{-3} to 10^{-4}N). He has related the ability of these species to block active sites to their theoretical values of binding strengths, crystal lattice energies, and heats of hydration.

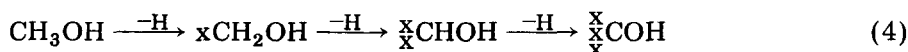
Oxidation mechanisms

A 'parallel-paths' reaction scheme for methanol oxidation has been proposed by Breiter [8]:



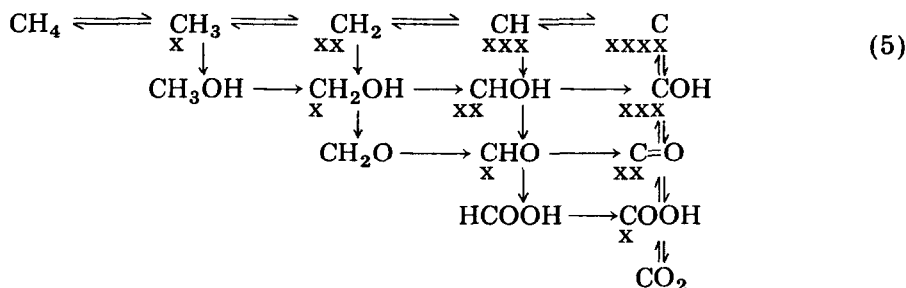
Traces of formaldehyde and formic acid have, indeed, been identified in solution, but the simultaneous build up of poison (which can only be removed by reaction with H_2O or OH at high potentials) leads to a rapid diminution of the current. The Russian group has tended to favour the $\overset{\times}{\text{C}}\text{OH}$ intermediate as being the most probable product. It was shown by $\overset{\times}{\text{F}}$ rumkin and Podlovchenko [33] that methanol chemisorption on platinum is associated with a dehydrogenation of the methanol molecule. That this process involves the splitting of C-H bonds and the formation of new Pt-C and Pt-H bonds was then proposed [19, 21].

Bagotsky's group suggests a stepwise process [34, 35]



with the removal of the first hydrogen being rate determining. Hence $\overset{\times}{\text{C}}\text{COH}$ is practically the only chemisorbed species formed.

Recently, Bagotsky *et al.* [36] have proposed a generalised scheme for the chemisorption, electro-oxidation, and electro-reduction of simple organic compounds on platinum. The compounds form a series from methane to carbon dioxide (*via* methanol, formaldehyde, and formic acid) and may be oxidised or reduced *via* the intermediate pathways given below:

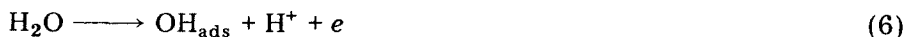


By assuming various reaction rates, it is possible to fit the observed data for methanol solutions into such a scheme and explain why only $\overset{\times}{\text{C}}\text{COH}$ is seen in significant amounts [9, 19, 26, 37 - 39]. It has been suggested that the chemisorbed particles of $\overset{\times}{\text{C}}\text{COOH}$ observed during formic acid adsorption [40] may be transformed to $\overset{\times}{\text{C}}\text{COH}$ at cathodic potentials *via* an interaction with adsorbed hydrogen [31, 41]. Indeed Adzic *et al.* [42] have suggested that in the promotion of Pt for formic acid oxidation, the role of adlayers of second metals is to suppress hydrogen chemisorption. This, in turn, retards the reaction of $\overset{\times}{\text{C}}\text{COOH}$ with adsorbed H to form the more tenaciously held $\overset{\times}{\text{C}}\text{COH}$.

It has been noted that the adsorption of oxygen on noble metals is generally stronger than that of other species and inhibits oxidation reactions [43]. Figure 2 shows results from a linear potential sweeping experiment for platinum in a methanol-sulphuric acid electrolyte. A rising current due to methanol oxidation is observed between 0.7 and 0.9 V [44]. The oxidation reaction does not occur on the electrode surface until both methanol and an oxygen-containing entity are adsorbed simultaneously. Beyond 0.9 V the oxidation reaction is inhibited as oxygen species are adsorbed in preference to methanol. At potentials more anodic than 1.2 V methanol may be oxidised on the oxide surface [45] and finally, at 1.6 V, oxygen evolution occurs. On the negative-going sweep, methanol does not re-adsorb in significant amounts until some of the oxide has been reduced (*i.e.*, below 0.8 V) and then another oxidation wave is observed. Once all of the oxide has been reduced the oxidation ceases again.

The surface coverage of organic adsorbate tends to drop to zero toward the beginning of the usual range of surface oxidation (*i.e.*, more anodic than 0.7 V) [46 - 49]. However, it is unclear from such measurements whether the oxide film forms through displacement or oxidation of the adsorbed organic molecules.

The importance of oxygen-containing species with regard to organic compound oxidation processes led Biegler [49] to make a close study of the oxygen adsorption reaction. His results showed that the charge transfer process in the region of methanol adsorption and oxidation involved the formation of adsorbed hydroxyl radicals [50]:



From the detailed structure of potential sweeps and ellipsometric measurements, Conway [51] also concluded that coverage by OH_{ads} occurs over this potential range. Biegler suggests that since OH_{ads} is present in such small percentages at the peak methanol oxidation current, then some precursor

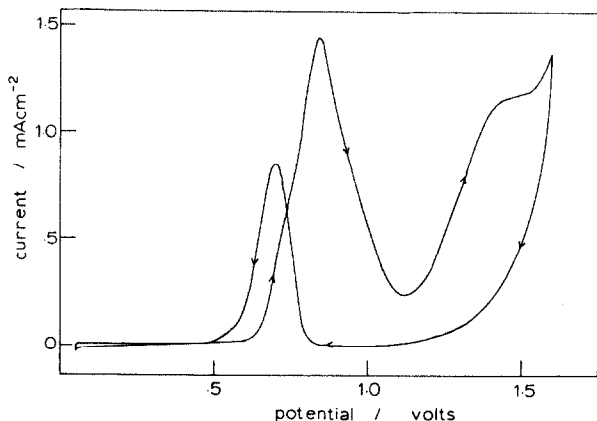
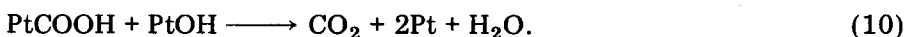
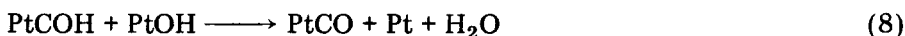
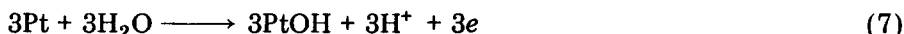


Fig. 2. Cyclic voltammogram for a smooth platinum electrode in 1M H_2SO_4 /1M CH_3OH at 23 °C. Potential measured against N.H.E. (Sweep rate = 10 mV s^{-1} .)

(such as an adsorbed water molecule) could be responsible for the removal of the residue. This view is supported by the kinetic isotope effects observed by Wieckowski [52].

Most oxidation schemes quoted assume the second reactant to be adsorbed hydroxyl [53, 54] groups, *e.g.*,



This assumption implies that for high steady state activity the catalyst must be bifunctional, *i.e.*, must adsorb both methanol and also OH species derived from the electro-sorption of water at low potentials.

Wieckowski and Sobkowski [55] on the other hand, have reported data which indicate that all platinum sites not occupied by the organic species take part in the oxidation, and that the surface oxidant should be $\text{H}_2\text{O}_{\text{ads}}$ rather than bulk H_2O as reported by others [31]. In support of this evidence, it has been shown that the oxidation of adsorbed species starts at a potential before OH_{ads} is formed. A layer of OH_{ads} forms from about 0.75 V and forms a monolayer by 1.1 V [56, 57]. The possible influence of adsorbed water has also been discussed by Janssen and Moolhuysen [58] and Andrew *et al.* [59].

Breiter has indicated [60] that the ageing of platinized platinum electrodes exerts a strong influence on the formation of the residue. Thus, a comparison of the results obtained by different investigators is only meaningful for electrodes with a similar surface reactivity. A study of the comparative oxidation of chemisorbed carbonaceous species obtained from methanol, formaldehyde, and formic acid led Breiter to conclude that at room temperature a similar species is formed in every case [61]. However, a common rate determining step in the electrochemical supply of oxygen for the oxidation of the intermediate could explain [62] the observed behaviour without having to assume the same net composition for the species produced from different initial molecules.

An analysis of the steady-state oxidation rate of methanol led Khazova *et al.* [63] to the conclusion that the adsorption and kinetic behaviour (and consequently the oxidation mechanism) do not differ qualitatively on platinized and smooth electrodes. Discrepancies in quantitative data have been attributed to varying states of electrolyte purity [64]. Activity measurements on smooth platinum (and, hence, of very low surface area) are of course extremely dependent on the impurity level in the electrolyte used. In sufficiently pure electrolyte solutions, current yields were found to be the same on smooth and platinized electrodes. It was also observed that the firmly adsorbed species remaining on the surface of the electrode after washing oxidises much more slowly than steady-state methanol oxidation

with CH_3OH present in solution. This has previously been attributed to electro-oxidation *via* a weakly bound species which could be removed by washing [65]. The possible transformation of chemisorbed species [66, 29] led to the suggestion that the intermediate may undergo an ageing process (perhaps by increased binding) and thereby become less active. This is borne out by evidence showing that the chemical composition of the residue is the same before and after washing [25, 67, 68].

Clearly there is still no widely accepted theory for the electro-oxidative processes occurring at platinum electrodes in methanol solutions. In summary, the most popular model at present consists of an adsorption process which obeys Langmuir kinetics initially but follows Elovich kinetics at higher surface coverages. This dissociative adsorption yields a strongly bound intermediate (probably of composition COH) that is susceptible to an ageing process and thus becomes less active. The oxidation most likely proceeds *via* a reaction involving either an adsorbed (possibly strained and therefore reactive) water molecule, or adsorbed OH species derived from the electro-sorption of water.

Related technological developments

In the search for improved electrocatalysts it has been shown that enhanced activity for organic oxidations over pure platinum can be obtained by the incorporation of other metals such as rhenium [69, 70], tin [69, 71, 72], ruthenium [73-76], osmium [77], rhodium [78], lead [42] or bismuth [42]. The performance improvements in the presence of these metals has been attributed to oxidation of the intermediate by oxygen-containing species which are associated with the added metal and are more reactive than those associated with platinum [79]. It is evident from cyclic voltammetry (Fig. 3 and ref. 80) that the metal additions encourage adsorption of OH species at much lower potentials than pure platinum. This supports the pro-

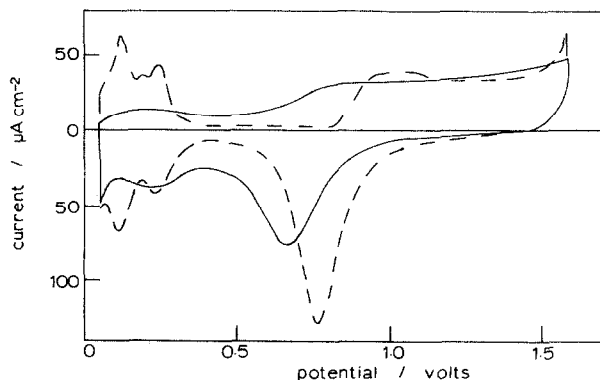


Fig. 3. Cyclic voltammogram for smooth Pt in $1\text{M H}_2\text{SO}_4$ before and after tin deposition. Potential vs. N.H.E. (Sweep rate = 50 mV s^{-1} , temp. = 23°C .) —, Pt/Sn catalyst. ---, Pure Pt catalyst.

posal that adsorbed OH is the agent responsible for residue removal. Another possible reason for the enhancement is that the methanol residue could be more weakly bound in the presence of the second metal. It has been suggested that these strongly bound ad-atoms are zero-valent and modify the adsorptive properties of platinum *via* a ligand effect [58, 72].

Considerable improvements are still required, however, before commercial viability (in particular for automotive applications) can be achieved. To date, only low power demonstration units have been constructed by Esso Research and Engineering [81] and Shell Research Limited [82], both in the early 1960's. Methanol-air fuel-cell batteries have been operated for over a year but the low electrical output and high catalyst costs made them a prohibitively expensive (several hundred pounds per kilowatt) source of energy. Recently Pt/Ru catalysts supported on pyrographite-coated carbon fibre paper have been reported with activities of 87 A g^{-1} at 0.4 V (in 1M $\text{CH}_3\text{OH}/3\text{M H}_2\text{SO}_4$ at 60 °C) [76]. This is about 400 times better than Pt Adams catalysts at the same potential. It seems now that more commercially attractive electrodes will be constructed from highly dispersed platinum-alloy catalysts and will probably be deposited on carbon supports along the lines described in refs. 83 - 85.

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