JOURNAL OF APPLIED ELECTROCHEMISTRY 10 (1980) 213–222

*The electrocatalytic oxidation of methanol in acid electrolyte: preparation and characterization of noble metal electrocatalysts supported on pre-treated carbon-fibre papers**

P. A. ATTWOOD, B. D. McNICOL, R. T. SHORT

Shell Research Ltd, Thorton Research Centre, PO Box 1, Chester, UK

Received 2 March 1979

The electrocatalytic aspects of direct oxidation of methanol in acid electrolyte in relation to fuel cell applications is briefly reviewed. The reaction requires noble metal catalysts (in particular platinum) in large quantities (several mg cm^{-2} of electrode area) to produce steady state current densities of commercial interest. Initial activities are about 10^4 times greater than steady state values, thus the problem in methanol electro-oxidation is to stabilize the initial activity.

The approaches generally taken are to develop methods of dispersing platinum more effectively, e.g. by depositing the metal on a conducting support, or to modify the properties of platinum by alloying it with a second component. The latter approach can have the effect of simply isolating platinum atoms from each other, thus limiting the size of the platinum clusters, or of electronically modifying the properties of platinum by virtue of the ligand effect of the second component in the alloy.

We have developed platinum and platinum–ruthenium catalysts supported on specially treated carbon-fibre paper which have substantially higher steady state activities than conventional catalysts. The method of preparation involves an ion-exchange procedure whereby noble metal cations become chemically bound to acidic surface oxide groups on the pre-oxidized carbon-paper surface. This produces platinum with increased surface area and high specific activity. It is proposed that the highly active form of platinum is involved in an interaction with the carbon support leading to improved performance. This modified form of platinum has been shown by cyclic voltammetry to have different characteristics of hydrogen adsorption/desorption and platinum oxide reduction from those of unsupported and conventionally supported platinum.

1. Introduction

The direct methanol–air fuel cell in which the fuel is dissolved in the electrolyte displays rapid start-up and instantaneous response factors that are particularly important when considering fuel cells for automotive applications. In terms of acceptability, availability and ease of distribution, methanol is an attractive fuel and is available from oil, natural gas or coal. However, methanol is, unfortunately, electrochemically relatively unreactive compared to, say, hydrogen or hydrazine and considerable progress in electrocatalysis is essential before realistic power densities for automotive applications can be achieved at an acceptable price. Nevertheless, since fuel cells produce electricity by means of galvanic oxidation they are not limited in their efficiencies by the Carnot cycle and with the increasing pressure to develop more efficient power sources for automotive and stationary applications there is a considerable incentive to develop the commercial methanol–air fuel cells. It is perhaps informative to compare the rating of a fuel cell powered vehicle with that of

---

*This paper was first presented at the meeting *Electrochemistry: Material Recovery and the Environment* held at the Thornton Centre, Chester in January 1979 and organized by the Electrochemistry Group of the Chemical Society.

0021-891X/80/020213-10$03.00/0

Table 1. Rating of fuel cell and battery-powered vehicles against internal combustion engined vehicles

Rated property	*Battery car*	*Fuel cell car*
emissions	much better	better
fuel economy	similar	much better
first cost	worse	worse
noise	better	better
driveability	better	better
power/weight ratio	much worse	worse
range	much worse	similar
running costs*	similar	much better
smoothness	better	better
durability	similar or better	similar or better

* On the assumption of parity in taxation on a thermal basis

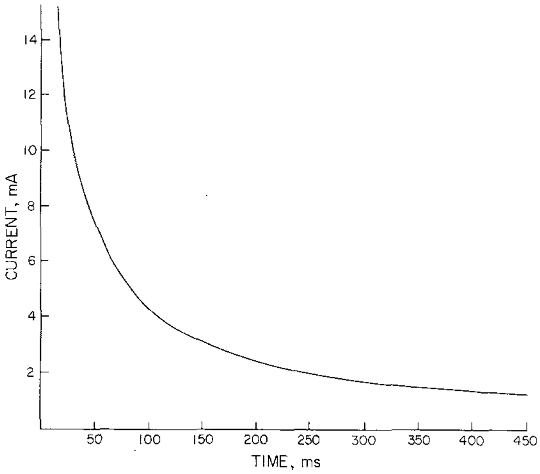


Fig. 1. Current–time profile for methanol oxidation on platinum foil in 3 M H_2SO_4 at 25° C and 0.44 V.

an internal combustion engined vehicle in areas of importance to both the community and the driver. Table 1 shows such a rating and a battery-powered vehicle is included for comparison. It can be seen that the fuel cell powered car has several significant advantages over both the internal combustion engined vehicle and the battery-powered vehicle. However, the areas where the developments will be required are those of cost and power-weight ratio, and both of these factors are connected with the poor reactivity of methanol.

The major problems barring the route to the commercial methanol–air fuel cell are essentially electro-catalytic. The requirement is for the development of cheap, highly active catalysts for both methanol and oxygen electrodes; both electrodes at the moment rely on noble metal catalysis and require considerable amounts of noble metal (platinum in particular). Whilst improvements in the performance of such fuel cells can be expected through engineering developments the overriding problem in low temperature methanol–air fuel cells remains catalytic. In this paper the problem of methanol electro-oxidation will be addressed.

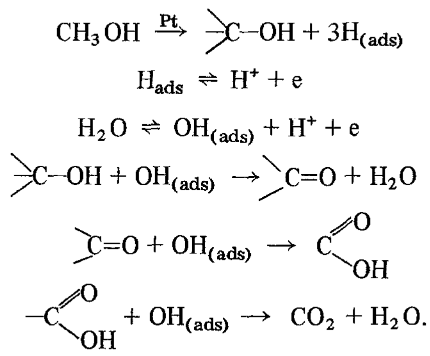
In an acid electrolyte the reaction can be formulated as

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e$$

whilst in alkali:

$$CH_3OH + 8OH^- \rightleftharpoons CO_3{}^{2-} + 6H_2O + 6e.$$

In acid electrolyte, which is generally used since CO_3^{2-} is formed in alkali, the reaction is catalysed only by platinum group metals and is characterized by very high initial catalytic activity, which rapidly decays to a much lower value within seconds (Fig. 1). After this initial fall in activity a further smaller drop in activity occurs over periods of hours under load. It is believed that the initial high activity, which is about 10^4 times greater than the quasi steady-state activity, arises from the dehydrogenation of methanol but this proceeds only to a limited extent and a dehydrogenated methanolic residue builds up on the catalyst surface leading to a large drop in catalytic activity. Further reaction of this poisoning residue occurs when adsorbed oxygen is present on the catalyst surface and this occurs on platinum at potentials largely anodic to the reversible methanol potential. A general scheme for the anodic oxidation of methanol in acid electrolyte has been proposed by Bagotsky *et al.* [1] as follows:



$$CH_3OH \xrightarrow{Pt} \gt C{-}OH + 3H_{(ads)} \tag{1}$$

$$H_{ads} \rightleftharpoons H^+ + e \tag{2}$$

$$H_2O \rightleftharpoons OH_{(ads)} + H^+ + e \tag{3}$$

$$\gt C{-}OH + OH_{(ads)} \rightarrow \gt C{=}O + H_2O \tag{4}$$

$$\gt C{=}O + OH_{(ads)} \rightarrow C\begin{array}{l}{/\!\!/}O\\ \diagdown OH\end{array} \tag{5}$$

$$-C\begin{array}{l}{/\!\!/}O\\ \diagdown OH\end{array} + OH_{(ads)} \rightarrow CO_2 + H_2O. \tag{6}$$

Current flows only as a result of Reactions 2 and 3. The reactions involving step-wise decomposition of the residue are all chemical in nature. An inspection of the reaction scheme indicates the requirements for an effective catalyst for methanol electro-oxidation, namely, the catalyst must be capable of adsorbing methanol and water at low potentials. Monometallic platinum meets the requirements for methanol adsorption but not for the electrosorption of water.

In searching for more effective catalysts the approaches generally taken have been either to modify platinum in the hope of improving its activity or to conduct an extensive search for non-noble metal compounds which are conducting and stable in acid electrolyte. The latter approach has been completely unsuccessful whilst the former approach has led to considerable developments in catalyst performance. The method of attack in trying to improve the activity is usually (a) to make more finely dispersed platinum, e.g. by supporting small particles of platinum on a conducting support such as carbon, or (b) to modify the properties of platinum by alloying it with a second component. Approach (b) can have the effect of simply isolating platinum atoms from one another, thus limiting the size of the platinum clusters, or of electronically modifying the platinum properties by virtue of a ligand effect of the second component. In this way platinum catalysts promoted by Ru [2–4], Sn [5–7], Re [8], Ti [9], Bi, Pb and Cd [10] were shown to produce improvements in quasi steady-state activity by up to two orders of magnitude.

For some time we have been actively involved in trying to improve the catalytic activity of platinum for this reaction and have developed both monometallic platinum and bimetallic platinum–ruthenium catalysts supported on a specially pre-treated carbon-fibre paper. The active catalytic species appears to be bound to the support in a chemical interaction that leads to the high activity. The platinum species also displays unusual adsorption characteristics that may play a

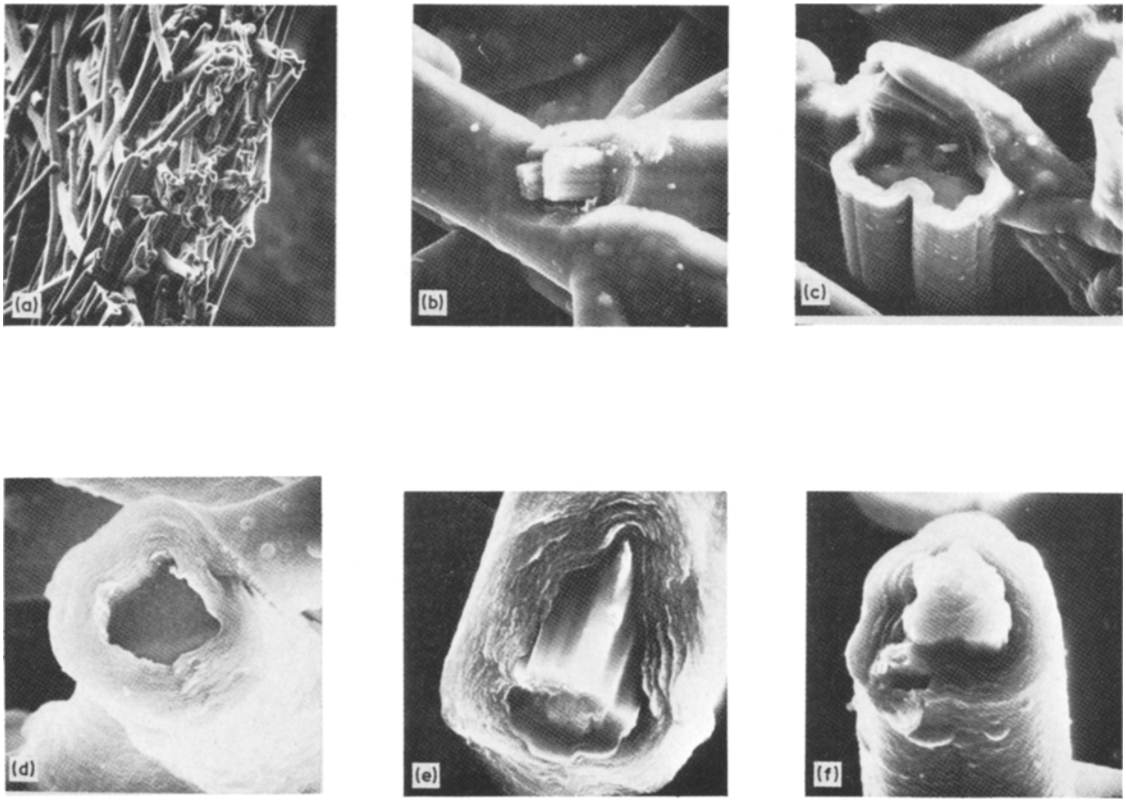


Fig. 2. End views of pyrographite coated carbon-fibre paper: (a) × 82; (b) × 825; (c) × 788; (d) × 1762; (e) × 2025; (f) × 1950.

role in determining the catalytic activity. This paper gives a detailed account of this work.

2. Experimental

2.1. *Catalyst support*

The support used was a Union Carbide pyrographite-coated carbon-fibre paper. This consists of a rayon-based carbon-fibre mat with bonding of the fibres by pyrographite (Fig. 2). The paper thickness was 0.25 mm and the BET surface area was $< 1\ \mathrm{m}^2\ \mathrm{g}^{-1}$.

2.2. *Support pre-treatment*

A possible route to the preparation of highly dispersed platinum which is chemically bound to carbon is via an ion-exchange interaction. However, to achieve this the carbon must be oxidatively pre-treated to produce acidic surface oxide groups [11] capable of interaction with cationic platinum salts. Therefore the carbon-fibre paper support was oxidized by two different methods, namely:

(a) Chemical oxidation by treating the support at 70° C with a solution of 10 wt% potassium dichromate in concentrated nitric acid. Treatment times varied between 0 and 360 min.

(b) Electrochemical oxidation by anodizing in a solution of 1% HNO_3 at a potential of 2 V and a current density of $1\ \mathrm{mA\ cm}^{-2}$ for periods between 0 and 180 min.

2.3. *Catalyst preparation*

The carbon paper support was ion-exchanged with Pt^{2+} through contact with a solution of $Pt(NH_3)_4(OH)_2$ of concentration $5\ \mathrm{mg\ ml}^{-1}$ for periods of up to 24 h. After exchange, the solution was removed and the catalyst was washed thoroughly with doubly distilled water to remove uncomplexed Pt ion. The catalyst was dried at 120° C for one hour and then heated in air at 300° C for one hour to decompose the complex platinum cation. Reduction of the catalyst was achieved by cathodizing the air-activated catalyst generally at $2\ \mathrm{mA\ cm}^{-2}$ and 60° C for 10 mins, in the electrochemical cell used for the activity determinations. Catalysts were also prepared by simple impregnation of either untreated carbon-fibre paper or the pre-oxidized material by soaking the support in a solution of $Pt(NH_3)_4(OH)_2$ of concentration $5\ \mathrm{mg\ ml}^{-1}$ followed by drying at 120° C and air activation at 300° C and electrochemical reduction, as for the ion-exchanged catalysts.

2.4. *Catalyst characterization*

2.4.1. Electrochemical measurements. The catalyst surfaces were characterized by cyclic voltammetry at room temperature using a PAR Model 175 Universal Programmer and a PAR Model 173 potentiostat/galvanostat equipped with a PAR Model 179 digital coulometer. The voltammograms were displayed on a Bryans Model 26000 A4 *x–y* recorder. Generally potentiodynamic cycling was carried out between 0 and 1.6 V (all potentials referred to a bubbling hydrogen reference electrode in the same solution). Platinum surface areas were determined coulometrically from the hydrogen desorption area of the anodic cyclic voltammetric sweep (0–0.4 V) assuming that $1\ \mathrm{cm}^2$ of Pt required $210\ \mu\mathrm{C}$ [12].

Polarization curves, a measure of catalyst activity, were measured galvanostically in 1 M CH_3OH/3 M H_2SO_4 at 60° C using a galvanostat built in this laboratory. Potential measurements were recorded 3 min after each current setting. The results are presented as plots of potential versus logarithm of the specific activity, specific activity being defined as the current flowing (in mA) per mg of platinum in the catalyst.

2.4.2. Catalyst analysis. Chemical analysis of the catalysts was carried out by extracting the Pt from the catalyst by boiling with aqua regia to dryness, dissolving the residue and analysing by atomic absorption spectrophotometry using a Perkin Elmer Model 305 Atomic Absorption Spectrophotometer.

2.4.3. X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed using an AE1-ES 200 spectrometer. Carbon 1s spectra were used in identification of carbon species whilst the $4f_{7/2}$ spectral line was used for identification of the Pt species.

3. Results and discussion

3.1. *Ion-exchange*

The loadings of platinum on the activated catalysts as found from analysis are shown in Table 2. As expected it was found that uptakes of Pt were highest when (a) the salt used in the exchange was cationic and (b) the substrate had been pre-treated to produce acidic surface groups. The uptake of Pt generally increased with the duration of the oxidizing pre-treatment (Table 2) and electrochemical oxidation led to the highest Pt loadings.

The oxidative treatment also had the effect of increasing the support surface area. The untreated carbon paper had a BET surface area of less than $1\ m^2\ g^{-1}$ which, with electrochemical or chemical oxidation, was raised to about $10\,m^2 g^{-1}$ for treatment times of one hour.

3.2. *XPS studies*

The surface of the uncatalysed carbon paper was examined by X-ray Photoelectron Spectroscopy (XPS). The results obtained from the oxidized carbon papers are given in Tables 3 and 4. The untreated carbon-fibre paper shows a carbon 1s peak at a binding energy of 285 eV, which is characteristic of hydrocarbon-type carbon with much weaker peaks at ~ 287 eV and 289 eV, corresponding respectively to carbon singly bonded and doubly

Table 2. Uptake of platinum by support during ion-exchange

Support pre-treatment	*Salt used in ion-exchange*	*Platinum loading* (mg)
None	$Pt(NH_3)_4(OH)_2$	< 0.01
None	H_2PtCl_6	< 0.01
5 min electrochemical oxidation	$Pt(NH_3)_4(OH)_2$	0.02
15 min electrochemical oxidation	$Pt(NH_3)_4(OH)_2$	0.05
30 min electrochemical oxidation	$Pt(NH_3)_4(OH)_2$	0.09
60 min electrochemical oxidation	$Pt(NH_3)_4(OH)_2$	0.15
90 min electrochemical oxidation	$Pt(NH_3)_4(OH)_2$	0.24
120 min electrochemical oxidation	$Pt(NH_3)_4(OH)_2$	0.24
180 min electrochemical oxidation	$Pt(NH_3)_4(OH)_2$	0.31
30 min $HNO_3/K_2Cr_2O_7$	$Pt(NH_3)_4(OH)_2$	0.04
45 min $HNO_3/K_2Cr_2O_7$	$Pt(NH_3)_4(OH)_2$	0.07
60 min $HNO_3/K_2Cr_2O_7$	$Pt(NH_3)_4(OH)_2$	0.09
120 min $HNO_3/K_2Cr_2O_7$	H_2PtCl_6	< 0.01

Table 3. Electrochemically oxidized carbon-fibre paper catalysts: hand deconvolution of carbon 1s spectra

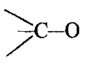
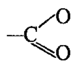
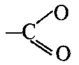
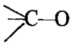
Catalyst	*Hydrocarbon-type carbon (binding energy 285 eV)* (%)	 *carbon binding energy 286.8 eV*	 *carbon binding energy 288.6 eV*
		Total (%)	
Untreated carbon support	72	28	
60 min electrochemical oxidation	50	50	
30 min electrochemical oxidation followed by ion-exchange with $Pt(NH_3)_4(OH)_2$ and air activation 300° C	75	25	

Table 4. $HNO_3/K_2Cr_2O_7$ treated carbon-fibre paper catalysts; deconvoluted carbon 1s spectra

Catalyst	*Hydrocarbon-type carbon (binding energy 285 eV) normalized intensity*	 *carbon (binding energy 288.6 eV) normalized intensity*	 *carbon (binding energy 286.8 eV) normalized intensity*
untreated carbon-paper support	80	5	15
support treated, 60 min at 70° C in $HNO_3/K_2Cr_2O_7$	51	26	22
support treated as above then ion-exchanged with $Pt(NH_3)_4(OH)_2$ and air activated at 300° C	63	19	18

bonded to oxygen [13]. On electrochemical or chemical oxidation of the support the intensity of both oxygenated carbon peaks increases with oxidation time (Tables 3 and 4) indicating that the treatment produces increasing quantities of such species. It is suggested that the spectra correspond to carboxylic acid and phenolic type groups on the surface of the carbon and that these groups are capable of ion-exchange with positive ions.

The spectra of the surface groups are reduced in intensity as a result of ion-exchange with $Pt(NH_3)_4(OH)_2$ and air activation, which suggests that the groups on the carbon surface are taking part in the attachment of the Pt to the carbon and may be destroyed in the process.

The Pt 4f spectra are shown in Figs. 3 and 4 for both electrochemically and chemically oxidized forms of the carbon. The catalysts which had been

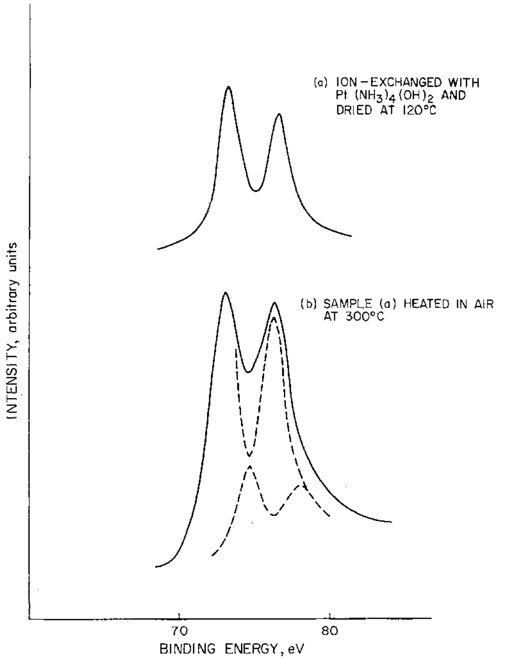


Fig. 3. Platinum 4f spectra of Pt supported on electrochemically oxidized carbon-fibre papers by ion exchange.

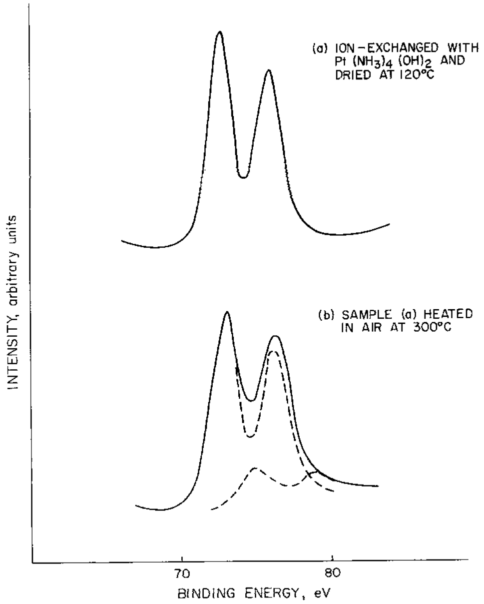


Fig. 4. Platinum 4f spectra of Pt supported on $HNO_3/K_2Cr_2O_7$ treated carbon-fibre papers by ion exchange.

ion-exchanged and dried at 120° C, i.e. without decomposition of the $Pt(NH_3)_4^{2+}$ cation, showed only one type of Pt species typical of Pt^{2+}, but after air activation at 300° C the platinum 4f spectra were different (Figs. 3 and 4). The doublets had abnormal spacings and relative intensities, which may be explained as a superposition of spectra from two Pt species both oxidized and corresponding in binding energy to species previously reported by Allen *et al.* [13]. The major component (75–80%) has a $4f_{7/2}$ binding energy of about 72.8 eV ascribed by Allen *et al.* to $Pt(OH)_2$, whilst the minor component (20–25%) has a binding energy of approximately 74.8 eV, as ascribed by Allen *et al.* to PtO_2.

3.3. *Catalytic activity*

The catalytic activities of the best catalysts prepared by ion-exchange of electrochemically anodized and $HNO_3/K_2Cr_2O_7$ treated carbon-fibre paper platinum, are shown in Fig. 5. The catalysts are about an order of magnitude higher in activity than the two commercial catalysts tested and about a factor of three more active than the best catalyst prepared using an impregnation technique.

The platinum loadings of the various catalytic electrodes are given in Table 5 along with the platinum metal surface areas. From Table 5 it appears that the best platinum dispersions are achieved with chemically pre-treated substrates and with some exceptions the lower the platinum loading the better is the platinum dispersion. A point to note, however, is the large variation in both platinum loading and platinum metal area between 1 cm^2 electrodes and 5 cm^2 electrodes. It seems that there is a considerable inhomogeneity in the distribution of platinum over the carbon surface.

3.4. *Electrochemical characterization*

Cyclic voltammetry showed that the catalysts prepared by ion-exchange have Pt surface areas in the region 60–200 $m^2\ g^{-1}$ depending on the substrate pre-treatment. With impregnated catalysts the metal surface areas were much smaller (30–70 $m^2\ g^{-1}$). In Fig. 6 the cyclic voltammetric profiles of an ion-exchanged supported Pt catalyst and an impregnated Pt catalyst are compared. The H adsorption/desorption regions are modified in so far as the structure normally found is smoothed out. There is a small peak on the anodic scan which appears only in catalysts supported on pre-oxidized carbon-fibre papers. We suspect that this peak arises from hydroquinone/quinone type groups on the carbon surface following Kinoshita and Bett [14]. It is apparent that the Pt oxide reduction peak which appears on the cathodic sweep occurs at 0.59 V for the exchanged catalyst and at 0.70 V for the impregnated catalyst. Moreover this peak occurs at about 0.75 V for unsupported Pt,

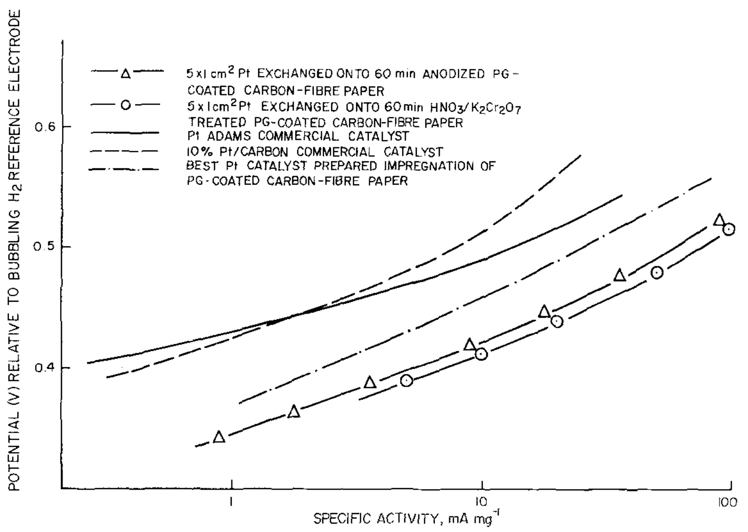


Fig. 5. Catalytic activity of Pt supported on pre-treated carbon-fibre paper by ion exchange: 3 M H_2SO_4, 1 M CH_3OH, temperature 60° C.

Table 5. Platinum loadings, surface areas and catalytic activities of single and composite catalysts

Catalyst	*Electrode size,* (cm^2)	*Metal surface area* (m^{2}g^{-1})	*Platinum loading,* (mg cm^{-2})	*Specific activity at 0.4 V* (mA mg^{-1})
Pt on 60 min electrochemically oxidized carbon paper	1	70	0.15	2.6
Pt on 60 min electrochemically oxidized carbon paper	5	104	0.11	5.4
Pt on 120 min electrochemically oxidized carbon paper	1	104	0.24	3.3
Pt on 120 min electrochemically oxidized carbon paper	5	74	0.26	2.4
Pt on 60 min $HNO_3/K_2Cr_2O_7$ treated carbon paper	1	66	0.09	1.6
Pt on 60 min $HNO_3/K_2Cr_2O_7$ treated carbon paper	5	149	0.04	7.3
Pt on 120 min $HNO_3/K_2Cr_2O_7$ treated carbon paper	1	–	0.03	6.0
Pt on 120 min $HNO_3/K_2Cr_2O_7$ treated carbon paper	5	209	0.02	5.8

Pt supported on untreated carbon-fibre paper and Pt supported on graphitized carbon. The profiles for these catalysts are shown in Fig. 7 where they are compared with the profile of an ion-exchanged Pt on treated carbon-fibre paper. Possibly the dispersion of Pt might influence the position of this peak. However Kinoshita and Bett [14] have published cyclic voltammograms of Pt supported on graphitized carbons with areas up to about 100 m^2 g^{-1} and in these cases the Pt oxide reduction peak occurs at about 0.75 V. Therefore we conclude that in our catalysts the electrochemical reduction of the Pt oxide layer is inhibited owing to the strong binding of Pt to the support. This interaction between carbon and the Pt may account for the higher activities of the carbon-fibre supported catalysts.

4. Conclusions

It is apparent from the XPS studies and the electrochemical characterization that the carbon sur-

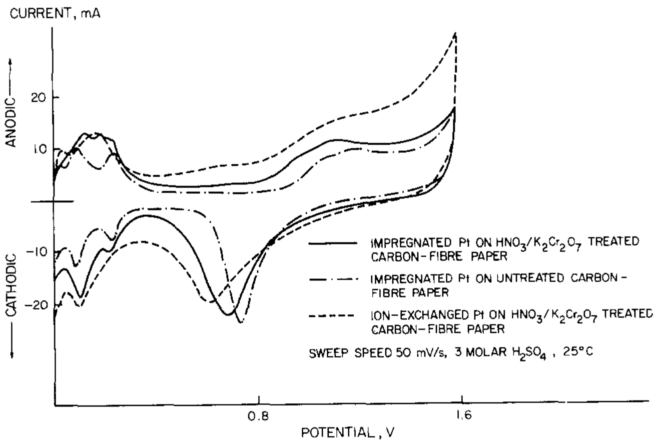


Fig. 6. Cyclic voltammograms of Pt supported on carbon-fibre paper.

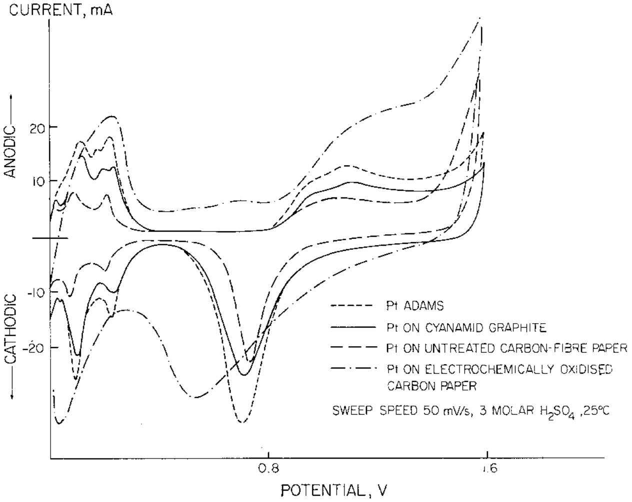


Fig. 7. Cyclic voltammograms of various Pt catalysts.

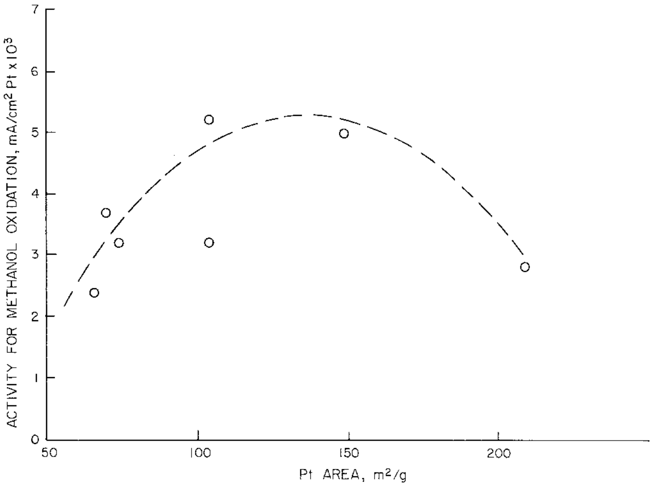


Fig. 8. Variation of the rate of methanol electro-oxidation per unit area of Pt with Pt specific area.

face groups play a role in complexing Pt and that after activation the Pt shows properties different from those of unsupported Pt by virtue of having higher specific activity and the oxide being more difficult to reduce electrochemically. The proposed interaction may be the origin of the enhanced rate of anodic oxidation of methanol, and if so, it is reasonable to expect that the activity per unit area of Pt would depend on the number of layers of Pt atoms between the metal–solution and carbon–metal interfaces, and hence would be a function of Pt crystallite size. The measured data have been examined in terms of the above proposal and the results are shown in Fig. 8. Despite the considerable scatter of the points in Fig. 8 it appears that the rate of methanol electro-oxidation (per unit area of Pt accessible to the solution) is a function of specific Pt area. It increases to a maximum as specific area increases but then falls. Very small crystallites may have reduced intrinsic activity but more data are essential before reliable conclusions can be drawn. Other workers have suggested Pt-support interactions [15, 16] to account for increased activity and it has been suggested [16] that Pt promotes activity of the support for the reaction involved as evidenced by a dependence of activity upon catalyst loading, however, no Pt surface areas were quoted in that work [16].

The XPS results indicated that most of the Pt existed as Pt^{2+} species after air activation with a small fraction of Pt^{4+}. It is likely that the Pt^{2+} is the species bonded to the support but the Pt^{4+} probably exists as free PtO_2. On electrochemical reduction in the test cell the PtO_2 would behave essentially as unsupported Pt and thus a small fraction of the Pt inventory is not present as highly active Pt. The presence of different amounts of free Pt over the carbon surface may account for the differing activities found for larger electrodes.

Thus by appropriate pre-treatment, platinum can be affixed to a carbon support chemically and upon activation and reduction a highly active catalyst results. The platinum is highly dispersed on the support and the electrochemical characterization reveals that the platinum is modified in some way by the support. The modification of the platinum is believed to be associated with the high activity found.

References

[1] V. S. Bagotsky, Yu. B. Vassil'ev and O. A. Khazova, *J. Electroanalyt. Chem.* 81 (1977) 229.

[2] H. Binder, A. Kohling and G. Sandstede, 'From Electrocatalysis to Fuel Cells' (edited by G. Sandstede) University Washington Press, Seattle (1972) p. 43.

[3] B. D. McNicol and R. T. Short, *J. Electroanalyt. Chem.* 81 (1977) 249.

[4] M. Watanabe and S. Motoo, *Ibid* 60 (1975) 267.

[5] K. J. Cathro, *J. Electrochem. Soc.* **116** (1969) 1608.

[6] B. D. McNicol, R. T. Short and A. G. Chapman, *J. Chem. Soc. Faraday I* 72 (1976) 2735.

[7] M. M. P. Janseen and J. Moolhuysen, *Electrochim. Acta* **21** (1976) 861.

[8] K. J. Cathro, *J. Electrochem. Tech.* **5** (1967) 441.

[9] M. M. P. Janssen and J. Moolhuysen, *Electrochim. Acta* **21** (1976) 869.

[10] R. R. Adzic, D. N. Simic, A. R. Despic and D. M. Drazic, *J. Electroanalyt. Chem.* **65** (1975) 587.

[11] V. L. Snoeyink and W. J. Weber Jr., *Progr. Surf. Membrane Sci.* 5 (1972) 63.

[12] T. Biegler, D. A. J. Rand and R. Woods, *J. Electroanalyt. Chem.* **29** (1971) 269.

[13] G. C. Allen, P. M. Tucker, A. Capon and R. Parsons, *ibid* **50** (1974) 335.

[14] K. Kinoshita and J. A. S. Bett, *Carbon* **12** (1974) 525.

[15] B. S. Hobbs and A. C. C. Tseung, *J. Electrochem. Chem.* **120** (1973) 766.

[16] V. S. Bagotsky, L. S. Kanevsky and V. Sh. Palanker, *Electrochim. Acta* 18 (1973) 473.