SHORT COMMUNICATION

# Performance of carbon-cloth bound porous-carbon electrodes containing an electrodeposited platinum catalyst towards the electrooxidation of methanol in sulphuric acid electrolyte

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## 1. Introduction

In recent years, there has been growing interest in the applications of fuel cells for motive power [1]. Direct methanol fuel cells (DMFCs) represent promising long-term systems for vehicular applications since the fuel is best transported and converted into energy from the liquid state [2]. However, the direct electrooxidation of methanol in solution involving conversion to an aldehyde, carboxylic acid and other intermediates before emerging as carbon dioxide, is very complex and requires a catalyst that is mainly platinum-metal based. With the continuing research and development efforts in fuel cell technologies, it has been possible to enhance the activity per unit weight of the platinum catalyst by dispersing it finely onto a high surface area active carbon support. Furthermore, the switch over from metal meshes to chemically inert but electrically conducting carbon papers that act both as back bones to the catalysed carbon providing the necessary mechanical strength to the electrode as well as current collectors, has ameliorated several materials related problems. More recently, with the advent of carbon cloths used as current collectors, the previous problems encountered with carbon paper such as fragility have been solved. This has also opened up newer avenues for better catalyst utilization.

In this communication we report a study on the performance of carbon-cloth bound porous-carbon electrodes containing platinum-catalyst dispersed chemically and those deposited electrochemically onto the active carbon support towards the electrooxidation of methanol in sulphuric acid electrolyte; the latter process besides being simpler is equally effective and to the knowledge of these authors is the first ever reported in the literature.

## 2. Experimental details

### 2.1. Fabrication of carbon-cloth bound porous-carbon electrodes

Vulcan XC-72 carbon pyrolysed at 930° C in a stream of $CO_2$ until a weight loss of 27% has been used during this study. Activated carbon (with or without the platinum catalyst) is suspended in Millipore conduc-

tivity water and agitated in an ultrasonic bath at 80° C for nearly 30 min. The resultant slurry is mixed with an aqueous suspension of PTFE binder (Fluon GP-2) and isopropanol under ultrasonic agitation at 80° C. In this manner, a putty-like mixture is obtained which is stretched and pressed onto a carbon cloth (E-Tek GC-14) current collector using a pressure of $200\,kg\,cm^{-2}$ for a period of 10 min followed by sintering at 350° C for 30 min. Electrodes of area $1.33\,cm^2$ were cut from this compacted sheet. The Teflon content in the electrodes is kept at 15 wt %. The weight per $cm^2$ of the electrodes including the cloth is about 20 mg of which carbon cloth amounts to about 11 mg and the thickness of the electrodes including the cloth is about 0.5 mm.

### 2.2. Electrodeposition of platinum-catalyst on the electrodes

The electrode was boiled in Millipore conductivity water for nearly 30 min prior to mounting into the holder with a water seal that provides an exposed area of $1\,cm^2$. The electrode holder that had provision for the current collector lead from the back of the electrode was then assembled into a three-electrode cell fitted with a platinum gauze counter electrode and a $Hg/Hg_2SO_4$, $SO_4^{2-}$ (MMS) reference electrode. The cell was then filled with a 0.02 M solution of chloroplatinic acid (Merck) that was purged with nitrogen and stirred mechanically. After purging of the chloroplatinic acid solution for nearly 30 min, the platinum-catalyst was electrodeposited onto the electrode under potentiostatic conditions (−0.3 V vs MMS). The amount of charge required to deposit the desired amount of platinum catalyst was monitored through a computer-controlled potentiostat (Oxsys Micros). During the deposition, the charge passed for the first 10 s was not counted by the programme as it is mainly consumed for charging the electrical double-layer on the carbon electrode and reducing any traces of oxygen.

### 2.3. Electrochemical characterization of electrodes towards methanol oxidation

The electrodeposited carbon electrode was washed with boiling Millipore conductivity water until free

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from any chloride content. This is of great importance as chloride ions are known to poison the activity of platinum to methanol electrooxidation [3]. The electrode was then mounted to an electrode holder similar to that described above and assembled into a three-electrode jacketed cell having a platinum gauze counter electrode and a MMS reference electrode. The cell was then filled with 2.5 M $H_2SO_4$ before being purged with nitrogen for about 1 h with constant mechanical stirring and the temperature maintained at 60° C. The nitrogen purging was then stopped and methanol added to give a 1 M MeOH concentration in the $H_2SO_4$ electrolyte. The galvanostatic polarization data on the electrode were obtained using the computer controlled Oxsys Micros system. The experiments were performed on several electrodes to ascertain the reproducibility.

### 2.4. *Chemical suspension of catalysts on activated carbon*

Carbon catalysed with an optimum loading of 15 wt % of platinum was prepared as described below. The desired amount of chloroplatinic acid stock solution ($10\,\mathrm{g\,dm^{-3}}$) was dispersed in a mixture of 190 ml of deionized water and 10 ml of isopropanol. To this mixture, activated carbon was added and the suspension placed in an ultrasonic bath for 5 min. The suspension was stirred for 30 min before the pH was adjusted to 7.0 with 0.1 M $KHCO_3$ solution. The suspension was then boiled for 1 h with continued stirring, after which an excess of 30% formaldehyde solution (Aldrich) was added, the suspension being further boiled for 1 h. At this stage, the orange

colouration from the dilute chloroplatinic acid was lost indicating complete reduction to the metal. The suspension was allowed to cool before filtration. The carbon residue was washed with copious quantities of boiling deionized water to remove chloride and any organics followed by overnight drying in an air oven at 70° C.

Carbon was catalysed with an optimum platinum–ruthenium bimetal loading as follows. Chloroplatinic acid stock solution was dispersed in a mixture of 290 ml of deionized water and 10 ml of isopropanol to give a 15 wt % platinum loading. To this, ruthenium(III)chloride was carefully dispersed to give a ruthenium loading of 7.5 wt %. To this mixture, activated carbon was added and the solution placed in an ultrasonic bath for 5 min. The suspension was then stirred for 30 min before the pH of the suspension was adjusted to 7.0 with 0.1 M $KHCO_3$ solution. The suspension was then boiled for 1 h with continuous stirring after which an excess of 30% formaldehyde solution (Aldrich) was added, the suspension being further boiled for 1 h. At this stage, the black colouration of the ruthenium(III)chloride was lost indicating complete reduction of both the chloroplatinic acid and the ruthenium(III)chloride to respective metals. The suspension was allowed to cool before filtration. The carbon residue was washed with copious quantities of boiling deionized water to remove chloride and any organics followed by overnight drying in an air oven at 70° C.

The electrodes were fabricated from these catalysed carbons and their performance towards oxidation of methanol was conducted as described in Sections 2.1 and 2.3, respectively.
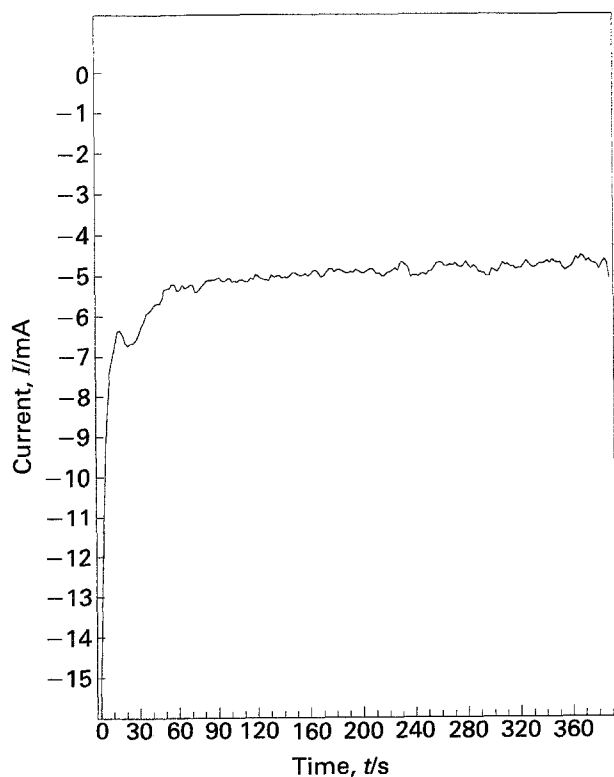


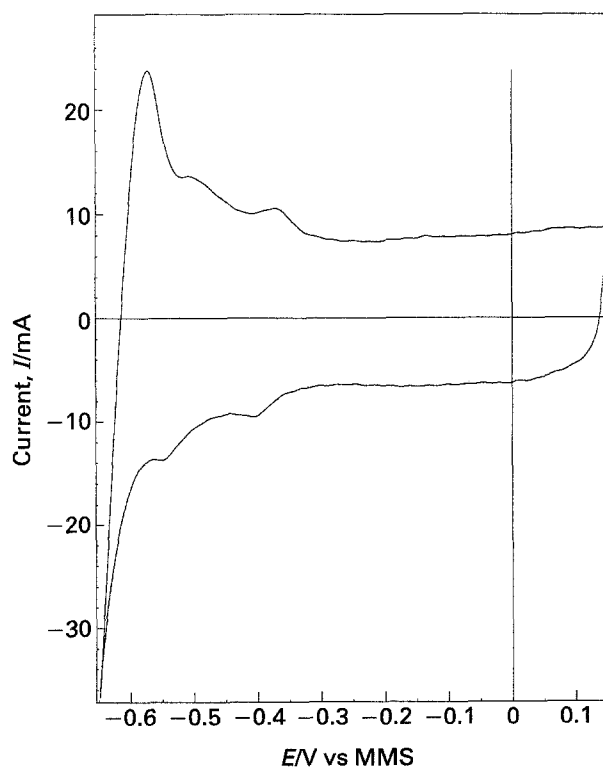Fig. 1. A typical plot of current as function of time during electrodeposition of platinum on carbon electrodes.



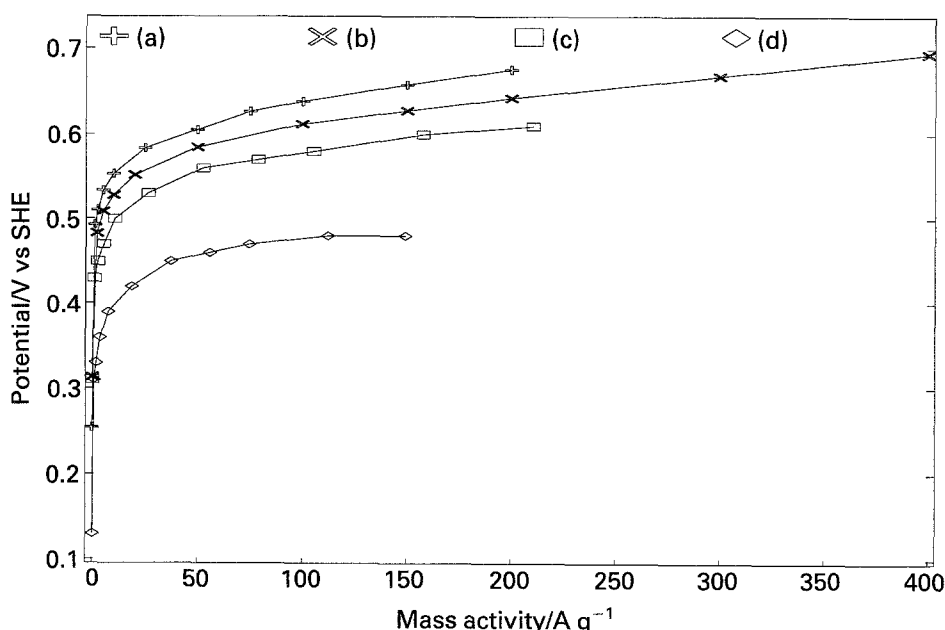Fig. 2. A typical cyclic voltammogram of platinized carbon electrodes in 2.5 M $H_2SO_4$ at 60° C (scan rate $20\,\mathrm{mVs^{-1}}$).

Fig. 3. Activity plots for various catalysed-carbon electrodes towards electrooxidation of methanol (1 M) in 2.5 M $H_2SO_4$ at 60° C: (a) 1 mg cm$^{-2}$ of platinum electrodeposited, (b) 0.5 mg cm$^{-2}$ of platinum electrodeposited, (c) 1 mg cm$^{-2}$ of platinum deposited chemically, and (d) (1.32 mg Pt + 0.66 mg Ru) cm$^{-2}$ deposited chemically.

## 3. Results and discussion

Figure 1 shows a typical plot of current as function of time during the electrodeposition of platinum on the carbon electrode. The current (cathodic) is seen to decrease rapidly until reaching a steady value of ~ 5 mA to the end of deposition. The cyclic voltammogram of the electrodeposited platinum electrode in 2.5 M $H_2SO_4$ at 60° C given in Fig. 2 shows the well known features of hydrogen adsorption/ desorption for platinum metal but is accompanied by the relatively large electrical double-layer charging/ discharging currents. The oxide features are not seen since the sweep is reversed before the potential for oxidation of platinum is reached. This also avoids any oxidation of carbon. The fact that it is possible to see clear features of platinum metal with cyclic voltammetery further affirms the absence of chloride ions that are known to be catalytic poison [3].

The galvanostatic polarisation data towards methanol (1 M) oxidation both on electrodeposited and chemically deposited platinum-catalysed porous carbon electrodes in 2.5 M $H_2SO_4$ at 60° C are shown in Fig. 3. The potentials are $iR$-corrected and are plotted against their mass activities. Both types of electrode seem to be quite similar in performance upto the loading current of 200 mA cm$^{-2}$. However, the activities attainable with electrodeposited carbon electrodes containing 0.5 mg of the platinum catalyst per cm$^2$ are substantially higher in relation to those with platinum loadings of 1 mg cm$^{-2}$. The particle sizes of the platinum particles as obtained from X-ray diffraction peak broadening and application of the Debye–Scherrer equation [4] are found to be 12 nm and 6 nm for electrodeposited and chemically dispersed platinum loadings, respectively.

Since the surface area of the particles are known to

be inversely proportional to their size, the surface area of the electrodeposited platinum electrodes will be half the value for the chemically deposited electrodes. Accordingly, the electrochemical activities of the chemically deposited electrodes should be twice the activity of the electrodeposited platinum electrodes. Indeed, this is observed since a polarization of 0.58 V vs SHE corresponding to the mass activity of 100 A g$^{-1}$ for the chemically deposited platinum electrode compares to mass activities of 50 A g$^{-1}$ and 25 A g$^{-1}$ for the electrodeposited electrodes with 0.5 mg cm$^{-2}$ and 1 mg cm$^{-2}$ platinum loadings respectively (Fig. 3). This indicates that platinum particles formed electrochemically have nearly the same surface activity as the chemically deposited platinum.

We have also examined the performance of a Pt–Ru bimetal catalyst towards the electrooxidation of methanol since ruthenium is known to increase the catalytic activity of platinum under similar conditions [5, 6]. A substantial improvement in the performance towards electrooxidation of methanol is exhibited by the carbon electrodes containing chemically deposited Pt–Ru catalyst in relation to the platinised carbon electrodes. At present, attempts are being made to electrodeposit optimum amounts of these bimetals on the carbon-electrodes.

## 4. Conclusions

The present study demonstrates that it is possible to fabricate electrodeposited platinized-carbon electrodes that besides being simpler in their production, are equally efficient towards the oxidation of methanol. The use of carbon-cloth as a current collector provides substantial improvements in mechanical strength over the carbon-paper based electrodes.

## Acknowledgements

## References

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