Carbon (CDX-975) based Pt electrodes for direct methanol fuel cell applications

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Normally, carbon materials, especially, Vulcan XC 72 are used as supports for Pt for the electrodes in fuel cells. The use of CDX 975 (a product of Columbian Chemical Company, Georgia) for support for electrode applications in methanol fuel cell is described here. The effect of the extent of Pt loading and the performance of various electrodes in methanol oxidation reactions has been studied. It is shown that 10% Pt is the optimal loading for electrode applications.

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Direct methanol fuel cell (DMFC) has received considerable attention as a leading candidate for portable power source of the future due to its high energy-conversion efficiency, easy storage of the liquid fuel, ambient operating temperature and simple construction1. The development of active anode is of primary importance in DMFC. Platinum based catalysts are promising candidates for anode electrocatalyst for DMFC applications. The presence of Pt appears to be necessary in the DMFC anode due to its excellent dehydrogenation properties at low temperatures. The electro-oxidation process of methanol to CO2 occurs through an initial dehydrogenation step2. Various attempts have been made to reduce the Pt content in the DMFC anode electrode. Ultra-low Pt loading electrodes (0.1 mg/cm2) have been developed for DMFC application3. Even though Pt has been demonstrated as the only active and stable noble metal for methanol oxidation, particularly in acid medium, pure platinum is readily poisoned by CO-like intermediates of the oxidation of methanol4. The convenient way to overcome CO poisoning is to employ Pt alloy with oxophilic metals, which would function as the sites for oxygen containing intermediate species, and promote their oxidation5.

Unsupported and supported Pt-Ru bimetallic catalysts6 have been investigated for methanol oxidation. In DMFC, interest has been focused on the development of suitable support material in order to increase utilization of noble metal catalysts. Carbon is widely used as support material for anode electro catalyst7-9. Polymers like polyaniline, polypyrrole, poly-3-methylthiophene, poly-3-ethylenedioxythiophene and composites based on polymers have also been studied as support for metal catalysts10-12. Pt-Ru bimetallic catalyst has been extensively examined as anode for DMFC applications. Recently, Pt-Ru prepared on a HY zeolite supported system has been found to be active for methanol oxidation13. Pt-Ru-Nafion [Pt/Ru(1/1): Nafion = 63.6:36.4, wt.%] electro-catalyst for the electro-oxidation of methanol has been investigated and the optimum composition of Nafion ionomer determined to be 30-40 wt.% to improve the fuel cell performance14. Oxidation of methanol at a Pt-Ru/Ti mini-mesh15 and PtSn/C16 anode has also been investigated. Other than carbon, carbon nanotubes (CNT), nanofibres and mesoporous carbon have been used as support for both Pt and Pt-Ru catalysts for methanol oxidation17-19. Also, Pt-Ru and Pt-WO3 supported on CNT have been used as possible electro-catalysts for methanol oxidation20.

Various reducing agents have been used to prepare Pt loaded carbon catalysts such as, hydrazine, formic acid, sodium formate and formaldehyde21-23. Formaldehyde reduction method is widely used to prepare noble metal electrodes for application in fuel cells and this method has the advantages of preparing...
Pt particles of uniform size without introducing impurity\textsuperscript{24}. The main reason for using this method is that the reduction potentials of the various metal ions (namely, Ru\textsuperscript{2+} to Ru is 0.455 V, Rh\textsuperscript{2+} to Rh is 0.6 V, Pd\textsuperscript{2+} to Pd is 0.951 V and Pt\textsuperscript{2+} to Pt is 1.188 V) are appropriate for reduction by formaldehyde. Formaldehyde oxidation results in various species, which can reduce the different metal ions of the same valence state, or metal ions of different oxidation states.

Among the available carbon supports, Vulcan XC 72 (cabot) has been extensively used. However, there is yet another carbon CDX 975 which has similar colloidal properties as Vulcan XC 72. The sulphur level in CDX 975 (0.6\%) is lower than that in Vulcan XC 72 (1\%). Also, impurity metals such as Na, K, Fe, etc., are considerably lower than what is present in Vulcan XC 72. Keeping that in view, this alternate carbon material has been investigated as support for electrode applications.

We have used formaldehyde as a reducing agent and CDX-975 as catalyst support for the preparation of Pt/CDX-975 as anode catalyst systems for possible DMFC applications. We have varied the loading of Pt between 5\% and 40\% in the catalyst. The objective of this study is to evaluate the use of CDX-975 (a carbon material marketed by Ms Columbian Chemicals Company) as a possible alternative support for fuel cell electrodes.

Materials and Methods

Formaldehyde, NaOH and sulfuric acid were obtained from CDH (Central Drug House, New Delhi). Hexachloro platinic acid (H\textsubscript{2}PtCl\textsubscript{6}) was obtained from Arora Mathew, Kolkata, methanol was obtained from Sisco Research Laboratory. Nafion 5\% solution (from Aldrich) was used as received. Glassy carbon was polished with fine alumina powder and ultrasonicated in water prior to use.

The Pt content on the catalyst/electrode was analyzed by Perkin-Elmer UV-Visible spectrometer, after calibration with standard solution containing known amount of metal. The metal was extracted from the catalyst/electrode by boiling in aqua regia. Shimadzu XD-DI X-ray diffractometer with Cu K\textsubscript{a} radiation was used to analyze the phase and crystallinity of the samples. The methanol oxidation activities of the materials were measured at the scan rate of 25 mV/sec using BAS Epsilon Cyclic Voltameter.

The electrodes (Pt/C) used in this study were prepared by formaldehyde reduction method. In formaldehyde reduction method, appropriate amount of carbon was dispersed in distilled water and required amount of 5\% H\textsubscript{2}PtCl\textsubscript{6} was added to it. pH of the mixture was adjusted to 10-11 using 0.1 M NaOH and required amount of 20\% formaldehyde solution was added. The above mixture was heated at 343 K for one hour under constant stirring. It was then washed thoroughly with distilled water, filtered and dried in hot air oven at 393 K for 4 h.

The electrodes for the electrochemical measurements were fabricated by dispersing the platinum loaded catalyst in 0.5 mL deionised water, 5 micro liter of 5-wt\%. Nafion solution was added and ultrasonicated for 20 min. A known amount of suspension was added on to the glassy carbon (GC) electrode and the solvent was slowly evaporated, resulting in Pt/CDX-975 on the GC electrode.

Results and Discussion

X-ray diffraction patterns of the catalysts prepared by formaldehyde reduction method are shown in Fig. 1(a-d). 20\% Pt/CDX-975 and 40\% Pt/CDX-975 samples exhibit characteristic peaks for the (111), (200), (220) and (311) planes of Pt at 20 values around 40, 47, 67 and 83, respectively, which corresponds to the fcc structure of Pt (JCPDS, card 4-802). These peaks are not observed for the 5\% Pt loaded carbon samples. For the 10\% Pt/CDX-975 sample, a broad peak is observed at 20 value of 44 corresponding to the (111) plane of platinum. This is due to the very small particle size of the supported Pt metal at low loadings. The average particle sizes of the catalysts have been determined from the peak at 20 = 40 using Scherrer’s equation\textsuperscript{25}. The values of the average particle size for all catalysts are presented in Table 1. The lowest particle size (< 2 nm) is obtained for 10\% Pt/CDX-975 sample.

Electro-catalytic measurements were made with BAS Epsilon Potentiostat. Three electrodes cell consisting of the GC working electrode (0.07 cm\textsuperscript{2}), Pt foil counter electrode (1 cm\textsuperscript{2}) and Ag/AgCl electrode as the reference electrode was used. Electrochemical measurements were carried out in 1 M CH\textsubscript{3}OH +1 M H\textsubscript{2}SO\textsubscript{4} aqueous solution.
Evaluation of electroactive surface area (EAS)

Cyclic voltammetry was employed to obtain electro-active surface area of the electrode materials in order to account for the higher current response in methanol oxidation. Figures 2a-2d show the cyclic voltammogram obtained in 1 M H₂SO₄ between −0.25 and 1.2 V vs Ag/AgCl (saturated KCl) at a scan rate of 25 mV/sec for Pt/CDX-975. Hydrogen adsorption and hydrogen desorption peaks appeared between −0.2 and 0.1 V in all the prepared catalysts and the columbic charge for hydrogen desorption (\(Q_H\)) was used to evaluate the active Pt surface area of the electrodes. The value of \(Q_H\) was calculated as the mean value between the amounts of charge exchanged during the electro adsorption (\(Q'\)) and desorption (\(Q''\)) of hydrogen on Pt sites\(^2\). The electrochemical active surface areas [EAS] for all electrodes were calculated using Eq. (1)\(^2\) and are presented in Table 1.

\[
EAS = \frac{Q_H}{[Pt]} \times 0.21
\]  

where [Pt] represents the platinum loading (mg/cm²) in the electrode, \(Q_H\) the charge for hydrogen desorption (mC cm⁻²) and 0.21 represents the charge required to oxidize a monolayer of hydrogen on bright Pt\(^2\). Higher value of electro-active surface area was obtained for 10% Pt/CDX-975 compared to other loadings such as 5%, 20% and 40% and this may be due to the lower particle size of the Pt which is observed from XRD data. The active surface areas of 20% and 40% Pt/CDX-975 obtained in this study are comparable to reported values for the catalyst prepared by formaldehyde reduction method\(^2\).
CHIDAMBARAM et al.: CARBON BASED Pt ELECTRODES FOR FUEL CELL APPLICATIONS

Fig. 2 — Cyclic voltammogram of Pt/CDX-975 in 1 M sulphuric acid: (a) 5% Pt/CDX-975, (b) 10% Pt/CDX-975, (c) 20% Pt/CDX-975, (d) 40% Pt/CDX-975.

Surface oxide formation at Pt/CDX-975

Pt is capable of forming platinum oxide in aqueous solution. The formation of platinum oxide is shown in Fig. 2b; the formed platinum oxide can be reduced reversibly. The potential of Pt-oxide formation is shifted towards the cathodic direction when Pt loading decreases.

Methanol electro oxidation activity

Cyclic voltammetry was carried out in 1 M sulfuric acid and 1 M methanol solution between -0.2 and 1.2 V at the scan rate of 25 mV/sec Vs Ag/AgCl(saturated KCl). Figures 3a-3d show cyclic voltammograms for all four catalysts namely 5%, 10%, 20% and 40% on CDX-975. Methanol oxidation peak observed at 0.788 V with peak current of 11.7 mA for 10% catalyst is higher than that of the other catalysts with the same geometry in the anodic sweep. The possible reason for higher current for 10% Pt/CDX-75 is due to the higher electroactive surface area and smaller particle size (about 2 nm) of the metallic particles. The percentage loading of platinum above 10% strongly influences the methanol oxidation potential. As the platinum loading increases, the peak potential is shifted towards anodic direction. The current densities obtained and the observed methanol oxidation potentials for all the catalysts are given in Table 2.

Effect of formaldehyde reduction

The cyclic voltammograms observed for methanol oxidation have been deconvoluted and are shown in Fig. 4(a-d). It is seen that methanol oxidation peaks can be resolved into three components and the current responsible for this observed activity of methanol oxidation has been attributed to oxidized form of Pt ions (Peak 1), Pt in the zerovalent state (peak 2) and the some Pt complex species (peak 3) generated from the oxidation products of formaldehyde used for the reduction of Pt ions from
Fig. 3 — Cyclic voltammograms of Pt/CDX-975 in 1 M sulphuric acid and 1 M methanol: (a) 5% Pt/CDX-975, (b) 10% Pt/CDX-975, (c) 20% Pt/CDX-975, (d) 40% Pt/CDX-975.

Fig. 4 — Deconvulated cyclic voltammogram of Pt/CDX-975 in 1 M sulphuric acid and 1 M methanol: (a) 5% Pt/CDX-975, (b) 0% Pt/CDX-975, (c) 20% Pt/CDX-975, (d) 40% Pt/CDX-975.
### Table 2 — Activity for methanol oxidation on Pt/CDX 975 untreated catalysts

<table>
<thead>
<tr>
<th>S.No</th>
<th>Catalysts</th>
<th>Forward scan</th>
<th>Reverse scan</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Potential (V)</td>
<td>Current (mA)</td>
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<tr>
<td>1</td>
<td>5% Pt/CDX-975 untreated</td>
<td>0.814</td>
<td>5.56</td>
</tr>
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<td>2</td>
<td>10% Pt/CDX-975 untreated</td>
<td>0.788</td>
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<td>20% Pt/CDX-975 untreated</td>
<td>1.072</td>
<td>9.98</td>
</tr>
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<td>4</td>
<td>40% Pt/CDX-975 untreated</td>
<td>1.160</td>
<td>10.25</td>
</tr>
</tbody>
</table>

### Table 3 — Percentage contribution of the various Pt species for the total observed activity for methanol oxidation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak I (%) Pt(ion)</th>
<th>Peak II (%) Metallic Pt</th>
<th>Peak III (%) Pt complex of oxidize product of HCHO</th>
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<tbody>
<tr>
<td>5% Pt/CDX-975</td>
<td>19.3</td>
<td>75.0</td>
<td>5.7</td>
</tr>
<tr>
<td>10% Pt/CDX-975</td>
<td>18.1</td>
<td>73.1</td>
<td>8.7</td>
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<tr>
<td>20% Pt/CDX-975</td>
<td>41.3</td>
<td>43.2</td>
<td>15.0</td>
</tr>
<tr>
<td>40% Pt/CDX-975</td>
<td>61.8</td>
<td>30.0</td>
<td>8.1</td>
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**Fig. 5** — Chronoamperometry response of electrodes in 1 M sulphuric acid and 1 M methanol: (a) 5% Pt/CDX-975, (b) 10% Pt/CDX-975, (c) 20% Pt/CDX-975, (d) 40% Pt/CDX-975.

H$_2$PtCl$_6$. All these species are found to be present in the electro-catalysts obtained and are active for the oxidation of methanol. It is seen from the data given in Table 3, that the extent of reduction of Pt ions decreases with Pt loading. It is, therefore, deduced that formaldehyde reduction method is appropriate for the preparation of Pt electro catalysts with low loadings.

**Chronoamperometry response of electrodes**

Stability of the electrode under potentiostatic conditions is essential for oxidation of methanol for the possible application in DMFC applications. This can be derived from plot of current Vs time behavior under potentiostatic condition in 1 M H$_2$SO$_4$ and 1 M methanol over a certain period of time. Current Vs time plot observed in 1 M H$_2$SO$_4$ and 1 M methanol for all the prepared catalysts for time period of 3 h are shown in Figs 5a-5d. It is seen that there is constant decay in the current with respect to time possibly suggesting the poisoning of the electrode by CO. For 10% Pt/CDX-975, though there is a gradual decay of current for a period of 4000 sec, the current appears to be stable afterwards, suggesting better tolerance of 10% Pt/CDX-97 (Fig. 5b) electrode compared to other catalysts. In conclusion, CDX-975 is a suitable carbon support for electrode applications and an optimum amount of Pt loading is required for use of this material as anode in DMFC.

**Acknowledgement**

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**References**