Polymer based oxidation catalyst for direct methanol fuel cell

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A polymer film on carbon electrodes is prepared by electropolymerisation of 1,5-dihydroxynaphthalene (1,5-DHN) in organic medium. The activity and stability for methanol oxidation follow the order: C/Poly(1,5-DHN)-Pt > C/Poly(1,5-DHN)/Pt > C/Pt. The higher activity and stability of the composite electrodes may be due to the dispersion of platinum particles in the polymeric environment.

Direct oxidation of methanol at the electrode surface is a topic of current interest, especially in the context of developing suitable electrode materials for Direct Methanol Fuel Cells (DMFC). Even though noble metals (either alone or in combination) have been examined for this application extensively, attempts are still on to effectively disperse these active species so as to derive maximum efficiency. Microparticles-dispersed polymer-modified electrodes have been recognized to have the necessary potential for application in DMFCs. Catalytic microparticles dispersed in an electrically conducting polymer matrices like poly-aniline, poly-pyrrole and poly (3-methyl) thiophene have been examined for methanol oxidation. Most of these electrodes fabricated by dispersing noble metals (single or in combination) have been shown to exhibit higher initial current densities (of the order of mA/cm²) which decrease with time due to either poisoning of the electrode surface or due to the destruction of the polymer surface because of higher temperature operation.

The polymer coated electrodes are usually prepared as thin films (typically a few hundred to a few μm thick) on gold or Glassy Carbon (GC) substrates by a number of techniques like drop or spin coating or by electropolymerization.

Synthesis of conducting polymers by electropolymerization of naphthol and its derivatives has been reported in the literature. In the present investigation 1,5-dihydroxy naphthalene (1,5-DHN) was electropolymerized under potentiostatic and potentiodynamic conditions in organic medium on carbon support. Since it has been suggested that the metal-polymer interaction is responsible for enhanced catalytic activity, it is presumed that the incorporation of platinum microparticles during the course of polymerization may lead to increased activity for the methanol oxidation. Three different electrodes were prepared. Firstly, Pt was electrodeposited during the course of polymerization. Secondly, Pt was electrodeposited on to the preformed polymer coated electrode. Thirdly, platinum was electrodeposited on bare carbon electrode. Electrooxidation was investigated on all these three electrodes and the activities of these electrodes have been compared.

Materials and Methods
Poly(1,5-dihydroxy) naphthalene (PDHN) was electrodeposited on stationary carbon electrode (1 cm²) (which had been pretreated by polishing with 0.5μm alumina powder followed by ultrasonification for 30 min to remove the residual alumina) from a solution containing 10^{-3} M 1,5-DHN (Loba Chemie) and 0.1 M lithium perchlorate (Merck) in acetonitrile (Merck) under constant potential (-0.35 V) and potential cycling (-0.2 to +0.9 V) against saturated calomel electrode (SCE). Pt foil (1.5 cm²) was used as the counter electrode.

The electrodeposition of platinum was carried under potentiostatic condition (-0.35 V/SCE) using 3.86 mM aqueous chloroplatinic acid (Hindustan Platinum Ltd) in acetonitrile using 0.1 M lithium perchlorate as the supporting electrolyte and Pt foil (1.5 cm²) as the counter electrode. The platinum electrodeposition was carried out on all the three electrodes. For the preparation of active electrodes, three different procedures were adopted: (1) Simultaneous polymerization and electrodeposition from 10^{-3} M 1,5-DHN and 3.86 mM aqueous chloroplatinic acid were carried out for three hours using 0.1 M LiClO₄/CH₃CN. (2) Platinum was deposited from 3.86 mM aqueous chloroplatinic acid
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Fig. 1 - Cyclic voltammograms for the electropolymerisation of $10^{-4} M$ 1,5-DHN in $1.0 M \text{LiClO}_4/\text{CH}_3\text{CN}$ cycled at 25 mV/s.

(3 hr.) on bare carbon electrode using 0.1M LiClO$_4$/CH$_3$CN on the preformed polymer coated electrode. (3) Platinum was deposited from 3.86 mM aqueous chloroplatinic acid (3 hr) on bare carbon electrode using 0.1M LiClO$_4$/CH$_3$CN. These electrodes were designated as C/Poly(1,5-DHN)-Pt, C/poly(1,5-DHN)/Pt and C/Pt.

Oxidation of methanol (2M) was studied on these three electrodes in 1.0 M $\text{H}_2\text{SO}_4$ using cyclic voltammetry and electrochemical measurements were performed using a Wenking Potentiocell POS 73 with a digital 2000 X-Y recorder. The molecular masses of poly (1,5-DHN) were determined by gel permeation chromatography using ultrasyrage column and Waters 410 differential refractometer. The columns were calibrated with polystyrene standards. The surface morphology of the poly(1,5-DHN)/C was examined by scanning electron microscopy (SEM JEOL 1500). The amount of Pt deposited was determined by UV-Vis spectrophotometry (Perkin-Elmer) and the absorbance was measured at 201.4 nm.

Results and Discussion

Typical cyclic voltammograms run at scan rate of 25 mV/s during the oxidation of 1,5-DHN and poly(1,5-DHN) film growth on carbon electrode are shown in Fig. 1. The broad peak at 0.83 V in the first anodic scan corresponds to the oxidation of 1,5-DHN and in the reverse scan, a cathodic process is evident which is indicative of the reduction of initially formed oxidized polymer. The second scan shows a current onset of +0.2V corresponding to the oxidation of poly (1,5-DHN) followed by monomer oxidation at +0.83 V. On repeated scanning, the increased current response of the polymer redox processes illustrates that the electrochemical polymerization is proceeding at the electrode surface to form a conducting electroactive film.

The cyclic voltammograms of poly(1,5-DHN) films at various scan rates in monomer free electrolyte solution were recorded to test the electroactivity of the polymer film. The values of potential of the anodic (+0.18V) and cathodic (+0.16V) processes are relatively close, indicating reversible nature of the redox process. Both anodic and cathodic peak currents are linearly proportional to scan rate, which suggests that electroactive polymer film is formed on the carbon support.

The redox potentials for the polymer are the same whether the polymer is obtained using cyclic potential sweep or under potentiostatic conditions. Fig. 2 shows the scanning electron micrograph of poly (1,5-DHN) on carbon support. A fibrillar morphology of the poly(1,5-DHN) is seen from the SEM photograph. The thickness of the polymer film is estimated to be of the order of 0.8 to 1.0 micron.

Table 1—Gel permeation chromatography results of poly(1,5-DHN) prepared under potentiostatic and potentiodynamic conditions

<table>
<thead>
<tr>
<th>Method</th>
<th>$M_M$ (Daltons)</th>
<th>$M_W$ (Daltons)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potentiodynamic</td>
<td>9561</td>
<td>13516</td>
<td>1.4136</td>
</tr>
<tr>
<td>Potentiostatic</td>
<td>9056</td>
<td>12035</td>
<td>1.3280</td>
</tr>
</tbody>
</table>
The values of number average, weight average molecular masses and polydispersity obtained by gel permeation chromatography for the poly(1,5-DHN) prepared under potentiostatic and potentiodynamic conditions are given in Table I.

The cyclic voltammogram of C/poly(1,5-DHN)-Pt electrode with ca. 430 μg platinum loading in 1M H₂SO₄ in the absence of methanol showed a redox peak at about -0.1V and a pair of redox peaks at about 0.7V. The pair of redox peaks at about 0.7V is due to the redox reaction of Pt/Pt(II) and the redox peaks at about -0.1V is related to the absorption and desorption of hydrogen on the Pt surface.

The cyclic voltammograms shown in Figs 3a-c correspond to the methanol oxidation on C/poly(1,5-DHN)-Pt (430μg), C/poly(1,5-DHN)/Pt (400μg) and ClPt (472 μg) electrodes in 2M methanol and 1M H₂SO₄. An oxidation peak at 0.64 V was observed during the positive potential sweep and the corresponding cathodic peak was observed during negative-potential sweep at about 0.44V. It is seen from Fig.3a that the methanol oxidation activity is higher in the case of platinum microparticle incorporated during the course of polymerization than that dispersed on to the preformed polymer coated C/Poly(1,5-DHN) and bare carbon (C/Pt) electrodes. It is clear from Figs.3a and 4 that the electrode where the platinum is incorporated during the course of polymerization, not only shows the initial higher activity but is also quite stable as compared to the other two electrodes (C/poly)1,5-DHN)/Pt and (C/Pt). The observation that activity of C/Poly(1,5-DHN)/Pt is higher compared to that of C/Pt suggests that the Pt particles appear to be stabilized when placed in polymeric environment. Another reason for the higher activity is that the active metallic species embedded in
Table 2—Comparison of methanol oxidation activity on composite and bulk platinum electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Onset potential (V) vs SCE</th>
<th>Peak current density (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/Pt</td>
<td>+0.20</td>
<td>9</td>
</tr>
<tr>
<td>C/Poly(1,5-DHN)-Pt</td>
<td>+0.15</td>
<td>14</td>
</tr>
<tr>
<td>C/Poly(1,5-DHN)/Pt</td>
<td>+0.10</td>
<td>25</td>
</tr>
</tbody>
</table>

polymer matrix are favourable sites for the activation of methanol and its subsequent oxidation.

It has been reported that methanol undergoes dissociative adsorption during oxidation14 leading to the formation of a series of adsorbed carboxyl intermediates such as (CH₃O)₅ (x=1-3) together with the formation of strongly bound adsorbed CO species. To further oxidize these intermediates to the final product CO₂, the adsorbate must react with the adjacent adsorbed oxygen containing species such as OHₐds or H₂O in aqueous solutions. Hence a good catalyst for the electrooxidation of methanol should easily adsorb methanol molecules, the dissociatively adsorbed intermediates and the oxygen containing species. The above results suggest that C/Poly(1,5-DHN)-Pt and C/Poly(1,5-DHN)/Pt possess the necessary sites for such simultaneous activation of various kinds of species.

Methanol is adsorbed on the platinum surface followed by the dehydrogenation of adsorbed species at lower potentials. As is evident from Table 2, the onset of methanol oxidation shifts negatively by 100 mV for C/Poly(1,5-DHN)-Pt and by 50 mV for C/poly(1,5-DHN)/Pt as compared to that for C/Pt. This suggests that the dehydrogenation of the adsorbed species is taking place at lower potential, this catalytic reaction leads to the rapid removal of the adsorbed hydrogen atoms from the platinum surface.

Thus this reaction is favoured by the dissociation of water to form adsorbed OH species by the removal of the adsorbed hydrogen atoms. Furthermore, the linearly adsorbed CO species reacts with adjacent adsorbed OH species forming CO₂. The proposed mechanism is speculative at this moment but further experiments are planned to substantiate these arguments.

The electrocatalytic activity and the stability of the electrode for the methanol oxidation follow the order: C/Poly(1,5-DHN)/Pt > C/Poly(1,5-DHN)/Pt > C/Pt. The higher activity and stability of C/Poly(1,5-DHN)-Pt and C/Poly(1,5-DHN)/Pt suggest that the platinum particles are stabilized in polymeric environment and the platinum-polymer interaction may be responsible for this.

References