Influence of sulphonic acid groups on enhanced anchoring of Pt to carbon black support and hence enhanced methanol oxidation activity

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Sulphonic acid groups have been introduced on Pt supported carbon black catalyst by two different methods, i. e., (i) alkyl sulfonic acid group incorporated on the carbon black support through diazotization step by the reaction of 2-aminoethanesulfonic acid and sodium nitrite in the presence of mineral acid and (ii) methylsulfonic acid group incorporated using sodium sulphite and formaldehyde. The prepared catalysts have been characterized by FT-IR, XRD, TGA, SEM, TEM and electrochemical methods. The catalysts prepared by both the methods have shown the redistribution of Pt nanoparticles on the carbon black support upon introduction of the sulphonic acid groups, along with enhanced activity for methanol oxidation. Among these two methods of sulphonation, the latter with sodium sulphite and formaldehyde has shown better performance and stability.

\textbf{Keyword:} Catalysts, Platinum catalysts, Sulphonation, Oxidation, Methanol oxidation

Among the energy conversion technologies, polymer electrolyte membrane fuel cells (PEFCs) fuelled by hydrogen and methanol are one of the front runners to replace the incumbent combustion engines mainly in transportation applications\textsuperscript{1}. Ambient operating conditions, easy handling and high energy density have made direct methanol fuel cells (DMFCs) a promising clean-energy source to portable fuel cell devices\textsuperscript{2,3}. However, the cost and durability of the technology still remains an issue despite significant effort for the past two decades, chiefly due to the use of expensive Pt as electrocatalyst in both anode and cathode\textsuperscript{4}. One strategy for reducing the cost is to decrease the amount of Pt loading by the efficient use of this metal\textsuperscript{5,6}. In this sense, the development of a new Pt based catalysts, with high electrocatalytic activity and improved active surface area utilization are critical for achieving the loading target\textsuperscript{7}.

In carbon supported Pt catalysts, the three phases, namely, the electron conducting carbon support, the proton conducting ionomer and the catalyst nanoparticle need to co-exist, for the electrooxidation to occur\textsuperscript{8}. Several efforts have been made to extend this three phase boundary to the inner pores of the catalyst support, to enhance the catalyst utilization. A major breakthrough was accomplished by the method based on impregnation of the traditional gas diffusion electrode with a solubilized Nafion ionomer\textsuperscript{9}. Further improvements on the electrode were made by Willson \& Gottesfeld\textsuperscript{10,11}, by mixing solubilized ionomer with a carbon supported catalyst to form a catalyst layer. However, these small carbon particles tend to agglomerate via intermolecular interaction between their surfaces\textsuperscript{12,13}; thus the platinum inside the agglomerated carbon structure cannot be utilized in electrochemical reactions\textsuperscript{14}. Studies were also conducted to understand if the carbon support itself can be made to conduct protons as well. Some studies in this direction using conducting polymer-polyanion composites as supports for catalyst have been reported\textsuperscript{15}. However, these composites lose their electronic conductivity soon in the acidic fuel cell working conditions. Studies on linking sulfonated silane on to a carbon supported catalyst\textsuperscript{16} showed better performance at lower Nafion content. However, with higher Nafion content, the modified catalyst shows lower performance than the unmodified one. This was explained due to the covering of the catalyst particles by the silane groups.

Creation of acidic carboxyl groups on the carbon support with nitric acid oxidation was also studied\textsuperscript{17}. However, because carboxylic acid is a weak acid and
a poor proton conductor, the increased performance was limited. Studies on grafting of polyacrylamide tertiary butyl sulfonic acid (PATBS) on Vulcan carbon support have reported a decrease of performance. This decrease in performance was attributed to the bulkiness of the ATBS molecule. Therefore, linking of shorter chain sulfonic acid groups was envisaged and study of grafting of methylsulfonic acid groups on to the carbon support of the catalyst particles was carried out by reacting with formaldehyde and sodium sulphite by the same group and an increase in performance was observed. Due to its small molecular size, the grafted sulfonic acid groups were able to penetrate into the small pores of the agglomerated carbon structure and so ensure the three phase boundary structure to the interior of the carbon particles. Chemically linked shorter chain sulfonic or phosphonic acid groups onto the carbon support of the supported catalysts through diazonium salts formed by reacting 2-aminoethanesulfonic acid or 2-aminoethanephosphonic acid with isobutyl nitrite was studied, and the resulting sulfonated catalysts showed better performance than the untreated counterparts. Another simple method to link sulfonic acid groups onto the surface of carbon particles functioning as catalyst supports was using ammonium sulfate as the sulfonating agent. However, these studies lack complete characterization of the prepared catalysts with respect to FT-IR and XRD analysis, and are studied mainly for electrochemical activities at different Nafion contents. Linking of phenylsulfonic acid on the Pt loaded carbon particles also has shown enhanced performance as reported by Selvarani et al. These reports were encouraging and prompted us to carry out study on linking of sulfonic acid groups on to the Pt loaded CDX975 (a commercial substitute to Vulcan 72) catalyst. Sulphonic acid modification was carried out by two different methods. (i) Grafting of ethylsulfonic acid group using 2-aminoethanesulfonic acid and sodium nitrite (Method 1) and, (ii) Grafting of methylsulfonic acid group using sodium sulphite and formaldehyde (Method 2).

**Materials and Methods**

**Loading of Pt on CDX975 carbon black support**

The Pt loading of CDX975 carbon black support was carried out by the hydrogen reduction method. Initially, the CDX975 carbon black was impregnated with the required quantity (for 10% Pt/CDX975) of the aqueous solution of 5 wt% hexachloroplatinic acid and stirred at 333-343 K, and evaporated to dryness. Then the reduction of platinum was carried out under the flow of hydrogen at 623 K for 4 h and the product referred to as unmodified catalyst.

**Sulphonic acid modification**

Sulphonic acid modification was carried out by two different methods.

**Method 1**: In a typical procedure using 2-aminoethanesulfonic acid and sodium nitrite, the unmodified catalyst was stirred with an aqueous solution of 10% or 20% of 2-aminoethanesulfonic acid and heated to 353 K. To this, 2 mL of conc. HNO₃ was added and treated at 353 K for 10 min. Then, it was cooled to room temperature and then further cooled to less than 283 K. To this, an ice cold solution of sodium nitrite was added and the reaction was carried out for 30 min. The solution was brought to room temperature, filtered, washed with warm distilled water and then dried in a vacuum oven at 343 K for 20 h. The catalysts thus prepared are designated as 10% or 20% 2-aesa-modified.

**Method 2**: The grafting of methylsulfonic acid group with sodium sulfite and formaldehyde was carried out in two steps. In the first step, the hydroxymethyl group was grafted on the carbon black support by the reaction of formaldehyde at the ortho position to the phenolic hydroxyl group. To the slurry of the Pt loaded carbon black catalyst in distilled water, formaldehyde and sodium sulfite were added and refluxed at 383 K for 12 h. After cooling to room temperature, it was washed with distilled water and protonated with 1 N HCl. It was further washed with distilled water and extracted with rotaevaporator to remove any sulfide by-products. Finally, it was dried at 338 K in a vacuum oven for 24 h. The catalyst thus prepared is represented as methylsulphonic acid modified.

The prepared catalysts were characterized by different techniques and their catalytic activity was evaluated for methanol electro-oxidation reaction.

**Characterization**

The pH measurements were made on a Elico pH meter, using aqueous slurry of the samples. The aqueous slurry of the sample was prepared by taking 30 mg of the sample in 7 mL of distilled water and ultrasonicated for 5 min. SEM images and EDAX were recorded using FEI, Quanta 200 instrument. The samples in the powder form were taken on the carbon tape and mounted on the SEM sample holder. X-ray
diffraction studies of the samples were carried out on Rigaku Miniflex(II) desktop X-ray diffractometer using Cu Kα (λ = 1.5405 Å), with Ni filter. The crystallite size was calculated by X-ray line broadening method using Debye-Scherrer equation. FT-IR spectra were recorded with Bruker FT-IR spectrometer by KBr pellet method at the resolution of 2 or 4 cm⁻¹. Transmission electron micrographs and high resolution transmission electron micrographs were recorded on a JEOL 3010 instrument. The samples (1-2 mg) were dispersed in 1-2 mL of acetyl alcohol by ultrasonication for 5 min and a drop of the dispersion was placed on a carbon coated copper grid and allowed to dry in air at room temperature.

Platinum was extracted from Pt/C catalyst by burning off carbon at 1073 K in air for 5 h and then Pt was first extracted with aqua regia (3 mL) thrice and then with conc. HCl (2 mL) twice. The extraction was made up to 25 mL with 2 M HCl. The extraction was estimated for Pt with inductively coupled plasma optical emission spectroscopy (ICP-OES).

Electrochemical measurements

The electrochemical studies were carried out with BAS Epsilon potentiostat. All the electrochemical measurements were performed with a three-electrode cell assembly, comprising a glassy carbon disk (dia. = 0.3 cm, geometrical surface area = 0.07 cm²) as the working electrode, Pt foil (1.5 cm²) as the counter electrode and Ag/AgCl as the reference electrode. Cyclic voltammetric studies for hydrogen adsorption/desorption charge determinations were conducted in 1 M H₂SO₄. Methanol oxidation and chronopotentiometric studies were carried out in 1 M methanol and 1 M sulphuric acid.

The working electrode was fabricated by dispersing 5 mg of the catalyst in 0.25 mL of distilled water by ultrasonication for 20 min. Then 10 μL of the dispersion was placed on 0.07 cm² of the glassy carbon electrode, and dried in air oven at 363 K for a few minutes. The resulting catalyst coating was covered with 5 μL of 5 wt% Nafion solution followed by drying in air for a few minutes.

Results and Discussion

The pH for the unmodified and sulphonic acid modified catalysts was determined. A decrease of pH (4.4 and 3.3 from 6.0) (Table 1) was observed with sulfoic acid modification, which is indicative of the incorporation of alkylsulfonic acid group on the carbon black support of the catalysts. The catalyst grafted with alkylsulphonic acid by Method 2 has shown a lower pH as compared to the one prepared by Method 1. This can be ascribed to the grafting of more sulphonic acid groups during Method 2 rather than by Method 1.

FT-IR spectra of unmodified and sulphonic acid modified samples are shown in Fig. 1. The spectra for the sulphonic acid modified catalysts show the symmetric stretching vibrations of S-O at 1100 cm⁻¹, which evidences the successful grafting of sulphonyl acid groups. It also shows broad intense band at 3200–3600 cm⁻¹, which can be attributed to the –OH vibration of sulphonic acid group. The less obvious –OH vibration for the catalysts modified by Method 1 can be attributed to the poor grafting of the sulphonic acid groups, which can further be attributed to the less reaction time in this method.

Figure 2 shows the XRD patterns of the unmodified and sulphonic acid modified catalysts. It shows the characteristic Pt peaks at 20 values around 40°, 46°, 68°, 81° and 86° corresponding to the (111), (200), (220), (311) and (222) planes of face centered cubic (fcc) structure of Pt (JCPDS card: 4-802). The diffraction peak at the 20 value around 25° corresponds to the (002) diffraction peak of CDX975.

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst</th>
<th>pH</th>
<th>Crystallite size of Pt nanoparticles (nm)</th>
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<tbody>
<tr>
<td>1</td>
<td>Unmodified catalyst</td>
<td>6.0</td>
<td>8.6</td>
</tr>
<tr>
<td>2</td>
<td>10% 2-aesa modified</td>
<td>4.4</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>20% 2-aesa modified</td>
<td>4.2</td>
<td>7.9</td>
</tr>
<tr>
<td>4</td>
<td>Methylsulfonylic acid modified</td>
<td>3.3</td>
<td>4.4</td>
</tr>
</tbody>
</table>

*From XRD data.
carbon black support. The average Pt crystallite size determined using Debye-Scherrer equation is given in Table 1. It shows decrease in particle size with sulphonic acid modification. A significant decrease in particle size of the catalyst modified by Method 2 is also observed. The slight decrease in particle size by Method 1 can be attributed to the poor sulphonic acid modification in this method, due to less reaction time compared to time taken in Method 2. In contrast, an increase in particle size upon sulphonic acid modification with ammonium sulphate was reported by Du et al., and was attributed to high reaction temperature. No change in Pt particle size was reported by Selvarani et al., for sulphonic acid modification similar to Method 1, using phenyl sulphonic acid. However, in this study, the decrease in Pt particle size upon sulphanonic acid modification can be explained based on the better anchoring nature of Pt nanoparticles by sulphonic acid groups. It is also supported by the values of weight percentage of Pt on the catalyst. The ICP analysis of the Pt extraction of the unmodified and sulphonic acid modified catalyst are shown in Table 2. It shows an increase in Pt percentage present in the catalyst upon sulphonic acid modification. It may be presumed that sulphonic acid groups on the carbon support anchor the Pt particles and decrease its leaching further. In other words, it can be said that sulphinic acid modification increases the stability of the carbon black supported Pt catalyst.

Figure 3 shows the TGA profiles in nitrogen atmosphere of the unmodified and the sulphonic acid modified (by Method 2) catalysts. It shows a weight loss due to the decomposition of the sulfonic acid group at around 150 °C for the sulfonic acid modified catalyst but not for the unmodified catalyst, as reported by Xu et al. and Du et al. This also supports the successful incorporation of sulfonic acid group. In addition, the sulphinic acid modified catalyst shows better thermal stability than the unmodified catalyst. This can be explained as due to the weak intermolecular hydrogen bonding between the sulphonic acid group and the quinone groups of the carbon black support, which keeps the carbon particles intact thus increasing thermal stability. Similar studies by Xu et al. and Du et al. have shown a decrease of thermal stability upon sulphonic acid modification. In this study, the better stability of the sulphonic acid modified catalyst is further evidenced by ICP analysis as explained earlier.

![Fig. 2](image2.png)  
Fig. 2 – XRD patterns of unmodified and sulphinic acid modified catalysts.

![Fig. 3](image3.png)  
Fig. 3 – TGA profiles of unmodified (curve 1) catalyst and sulphinic acid modified by Method 2 (curve 2) catalyst in N₂ at 10 °C/min.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt (wt%)</th>
<th>EAS (m²/g)</th>
<th>Peak current density (mA/cm²)</th>
<th>Mass specific methanol oxidation activity (A/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified 10% Pt/CDX</td>
<td>6.1</td>
<td>10.7</td>
<td>35.7</td>
<td>125</td>
</tr>
<tr>
<td>10% 2-aesa/10% Pt/CDX</td>
<td>7.0</td>
<td>9.3</td>
<td>78.6</td>
<td>275</td>
</tr>
<tr>
<td>20% 2-aesa/10% Pt/CDX</td>
<td>-</td>
<td>9.8</td>
<td>82.9</td>
<td>290</td>
</tr>
<tr>
<td>Methylsulphonic acid modified 10% Pt/CDX</td>
<td>10.0</td>
<td>41.5</td>
<td>138.4</td>
<td>484</td>
</tr>
</tbody>
</table>

*From ICP data.*
EDAX results of unmodified and sulphonlic acid modified catalysts show the absence of sulphur in the unmodified catalyst, but an increase in S content (0.04 % and 0.08 %) in the catalysts modified by Methods 1 and 2 respectively (Fig. 4).

Figure 5 shows the TEM images of the unmodified and sulphonlic acid modified (by Method 2) catalysts. It shows aggregated morphology for both Pt and carbon black particles before modification but uniform dispersion of smaller Pt nanoparticles after sulphonlic acid modification. The particle size of Pt nanoparticles determined from the images is found to be 8 and 4 nm respectively for the unmodified and sulphonlic acid modified catalysts, which is in close agreement with the XRD results and confirms the redistribution of Pt nanoparticles upon sulphonlic acid modification.

Electrochemical measurements

The cyclic voltammograms of the unmodified and sulphonlic acid modified catalysts in 1 M sulphuric acid show an increase in current density for hydrogen adsorption/desorption upon sulphonlic acid modification (Figure 6(a)). The CVs also confirm that the current density of the catalyst prepared by Method 2 is significantly higher than that by Method 1. The higher current density for the catalyst prepared by Method 2 can be attributed to the higher reaction time as explained earlier. The electrochemical active surface area calculated from the current density for hydrogen adsorption/desorption is listed in Table 2. It shows an enhanced electrochemical active surface area of the catalyst upon sulphonlic acid modification by Method 2. On the other hand, the electrochemical active surface area of the catalyst modified by Method 1 shows only a slight decrease as compared to that by the unmodified catalyst. This can be explained as follows: the cyclic voltammetric pattern of the catalyst modified by Method 1 is little different from that of a typical Pt catalyst. Even though the current density for hydrogen adsorption/desorption is higher than that for the unmodified catalyst, the charge for hydrogen adsorption/desorption is decreased, which may be attributed to the presence of Pt in higher valence states, in addition to the zero valence.

Figure 6(b) shows the methanol oxidation current density in 1 M methanol and 1 M H₂SO₄ of the unmodified and the sulphonlic acid modified catalysts. As given in Table 2, the sulphonlic acid modification shows a significant increase in activity for the sulphonlic acid modified catalysts as compared to that
Fig. 5 – TEM of (a) unmodified and (b) sulphonic acid modified catalyst by Method 2.

Fig. 6 – Cyclic voltammograms of unmodified and sulphonic acid modified catalyst at the scan rate of 25 mV/s in (a) 1 M H₂SO₄, and, (b) 1 M H₂SO₄ and 1 M methanol.

Fig. 7 – Cyclic voltammograms of unmodified and sulphonic acid modified catalysts in 1 M H₂SO₄ at the scan rate of 25 mV/s. [Catalyst prepared by (a) Method 1 and (b) Method 2].
of the unmodified catalysts. The increase in activity upon sulphinic acid modification, also reported by Xu et al.\textsuperscript{18} and Kuroki & Yamaguchi\textsuperscript{8}, can be attributed to two factors: (i) better dispersion/ redistribution of the Pt nanoparticles and (ii) the increased proton conductivity of the catalyst to the inner pores of the carbon black support. This result is supported by the deductions based on the pH, FT-IR and XRD studies discussed above.

The stability of the catalysts prepared by different methods have been studied by cyclic voltammetry with different cycles as shown in Fig. 7. The stability of the catalyst prepared by Method 1 (Fig. 7(a)) can be considered as good, since there is no decrease in current density with increasing cycles even up to 100 cycles. In the case of the catalyst prepared by Method 2 (Fig. 7(b)), the stability was attained very quickly in the initial cycles itself and did not decrease even after 50 cycles. The enhanced stability of the catalysts can be attributed to the binding of carbon particles through intermolecular hydrogen bonding due to the grafted sulphinic acid groups.

Conclusions

The grafting of alkyl sulphinic acid groups on Pt/CDX975 catalyst was carried out by two different methods, i.e., (i) through diazotization by the reaction of 2-aminoethanesulfonic acid and sodium nitrite in the presence of mineral acid, and, (ii) by reacting with sodium sulphite and formaldehyde. The prepared catalysts have been characterized by FT-IR, XRD, TGA, SEM, TEM and electrochemical methods. The sulphinic acid modified catalysts by both the methods show the redistribution of Pt nanoparticles on the carbon black support upon introduction of the sulphinic acid groups. The modified catalysts have been studied for methanol electrooxidation activity. The catalysts modified by both the methods show enhanced activity. The enhanced performance of the sulphonic acid modified catalysts can be attributed to two factors: firstly, better dispersion/ redistribution of the Pt nanoparticle, and secondly, the increased proton conductivity of the catalyst to the inner pores of the carbon black support. In addition to the methanol oxidation activity, the limited study of the stability of the catalysts also shows the significant enhancement in stability upon sulphinic acid modification of the Pt/carbon black catalyst.

References