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A phenyl-sulfonic acid anchored carbon-supported platinum catalyst for polymer electrolyte fuel cell electrodes

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Abstract

A method, to anchor phenyl-sulfonic acid functional groups with the platinum catalyst supported onto a high surface-area carbon substrate, is reported. The use of the catalyst in the electrodes of a polymer electrolyte fuel cell (PEFC) helps enhancing its performance. Characterization of the catalyst by Fourier transform infra red (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and point-of-zero-charge (PZC) studies suggests that the improvement in performance of the PEFC is facilitated not only by enlarging the three-phase boundary in the catalyst layer but also by providing ionic-conduction paths as well as by imparting negative charge to platinum sites with concomitant oxidation of sulfur present in the carbon support. It is argued that the negatively charged platinum sites help repel water facilitating oxygen to access the catalyst sites. The PEFC with modified carbon-supported platinum catalyst electrodes exhibits 40% enhancement in its power density as compared to the one with unmodified carbon-supported platinum catalyst electrodes.

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1. Introduction

In the post-oil energy economy, hydrogen-based fuel cells are being perceived as a possible energy alternative. Hydrogenbased polymer electrolyte fuel cells (PEFCs) are most promising as they offer an order of magnitude higher power density than any other fuel cell system. A PEFC is fed with hydrogen, which is oxidized at the anode and oxygen that is reduced at the cathode. The protons released during the oxidation of hydrogen pass through the proton exchange membrane to the cathode. The electrons released during the oxidation of hydrogen travel through the external electric-circuit generating an electrical current. Owing to the high degree of irreversibility of the oxygen reduction, even under open-circuit conditions, the over potential of the oxygen electrode in a PEFC happens to be about 0.2 V. This represents a loss of about 20% from the theoretical maximum efficiency for a PEFC. Accordingly, at the heart of a PEFC is the electrocatalyst that has to fulfill several requirements, such

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Usually, the electrocatalyst is supported onto a porous carbon support in order to increase its contact area with the reactants. Since both the electrons and protons are involved in the electrochemical reactions, the porous catalyst layer must conduct both of these species optimally [4]. Furthermore, to extend the three-phase boundary in the catalyst layer, the electrocatalyst needs to be dispersed with a proton conducting substance, such as Nafion. This has been shown to improve the performance of the PEFCs [5–8], but the platinum in the catalyst layer remains yet not fully utilized.

Uchida et al. [9,10] have studied the microstructure of the catalyst layer. During the catalyst preparation, nanometer-sized platinum particles are dispersed onto the surface of a 30–40 nm sized carbon support to enhance the platinum catalyst surface area. However, the small carbon particles tend to agglomerate due to the intermolecular interactions between their surfaces rendering the platinum sites within the agglomerate unutilized. This is because Nafion ionomer, generally added to the catalyst as a proton-conducting phase during the electrode fabrication

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process, fails to penetrate the small pores in the carbon agglomerate. Besides, Nafion often affects the efficiency of the platinum electrocatalyst by blocking the active sites restricting the gas permeability of the catalyst layer as well as its electronic conductivity. Accordingly, there is a limit on the quantity of Nafion that needs to be added without affecting the cell performance. In recent years, certain new approaches, such as the introduction of proton-conducting agents in the catalyst carbon support, have been adopted [11-14] to further the performance of PEFCs. Xu et al. [12] have reported sulfonation of carbon-supported catalyst using 2-aminoethane sulfonic acid. Yu and Kosbach [11] and Srinivas and Dotson [13] have introduced sulfonic acid groups to carbon support using various sulfonating agents. But, the aforesaid studies lack the characterization of sulfonic acid groups anchored to the carbon support, optimization in the concentration of sulfonic acid groups and its mechanistic investigation.

The present study provides a simple but an effective route to chemically anchor phenyl-sulfonic acid groups, using *p*-amino phenyl-sulfonic acid, onto the catalyst carbon support. Since X-ray photoelectron spectroscopy (XPS) can provide a better insight into the surface properties of the carbon-supported catalysts [15–19], such a study is also conducted in conjunction with electrochemistry. It is suggested that $Pt^{\delta-}$ -sites are produced in the catalyst accompanied by the oxidation of sulfur, which help repelling the water molecules from the active platinum sites in the catalyst layer and facilitate their participation in electrochemical reduction reaction, bringing about an enhancement in the PEFC performance.

2. Experimental

2.1. Preparation of carbon-supported platinum catalyst

A sulfito-complex route is adopted [20] to prepare 40 wt.% platinized carbon. The required amount of Vulcan XC-72R (Cabot Corporation) is suspended in distilled water and agitated in an ultrasonic water bath (Vibronics, 300 W, 250 kHz) to form slurry. The required amount of $Na_6Pt(SO_3)_4$ is dissolved in 1 M H₂SO₄ and diluted with distilled water. The solution is added drop wise to the carbon slurry with constant stirring at 80 °C followed by the addition of 30% H₂O₂ with the temperature maintained at 80 °C that results in vigorous gas evolution. The solution is further stirred for 1 h. Subsequently, platinized carbon is obtained by adding 10% formic acid solution, which is filtered, washed copiously with hot distilled water, and dried in an air oven at 80 °C for 2 h.

2.2. Anchoring phenyl-sulfonic groups to carbon-supported platinum catalyst using p-amino phenyl-sulfonic acid

Carbon-supported (VulcanXC-72R) platinum catalyst is mixed with hot aqueous solution of *p*-amino phenyl sulphonic acid (Merck, India) to form slurry. The required amount of concentrated nitric acid is added drop wise to the carbon slurry with constant stirring at 80 °C. The resulting suspension is cooled below 20 °C. Subsequently, the aqueous solution of sodium nitrite is added with stirring forming 4-sulfobenzenediazonim salts in situ that react with carbon support [21,22]. The mixture is stirred for 30 min, filtered, washed copiously with hot distilled water to remove the unbounded residues, and dried in an air oven at 120 °C for 2 h. In the subsequent text, the resulting carbon-supported catalyst is referred as modified catalyst and the initial carbon-supported catalyst is referred as unmodified catalyst.

2.3. Fabrication of membrane electrode assembly

Both anode and cathode comprise a backing layer, a gasdiffusion layer and a reaction layer. A Teflonised (15 w/o PTFE) carbon paper (Toray-TGP-H-090) of 0.28 mm thickness is employed as the backing layer in these electrodes. To prepare the gas-diffusion layer, Vulcan-XC72R carbon is suspended in cyclohexane and agitated in an ultrasonic water bath for 30 min. To this, 15 w/o PTFE suspension is added with continuous agitation. The resultant slurry is spread onto a Teflonised carbon paper and sintered in a furnace at 350 °C for 30 min. To prepare the reaction layer, the required amount of the catalyst (modified or unmodified) is suspended in isopropyl alcohol. The mixture is agitated in an ultrasonic water bath, and 7 w/o of Nafion (Dupont) solution is added to it with continuous agitation for 1 h. The resulting ink is coated onto the gas diffusion layer of the electrode. Both anode and cathode contain platinum loading of 0.5 mg cm^{-2} (active area 25 cm^2) that is kept identical for all MEAs. A thin layer of 5 w/o Nafion solution is spread onto the surface of each electrode.

Nafion-1135 (DuPont) membrane is boiled with 30 v/o nitric acid for 1 h followed by its copious rinsing and washing with distilled water. It is then boiled in 5 v/o H_2O_2 for 1 h followed by washing with distilled water. Finally, the membrane is boiled in 1 M H_2SO_4 for 30 min followed by its rinsing and washing in distilled water.

The membrane electrode assembly (MEA) is obtained by hot pressing the cathode and anode on either side of a pretreated Nafion-1135 membrane at 25 kN (~60 kg/cm²) at 130 °C for 3 min.

2.4. Electrochemical characterization

2.4.1. Design and polarization of PEFC single cells

MEA performance is evaluated using a conventional 25-cm² fuel cell fixture with parallel serpentine flow field machined on graphite plates (Schunk Kohlenstofftechnic). After equilibration, the single cell is tested at 60 °C with gaseous hydrogen at anode and gaseous oxygen at cathode at atmospheric pressure. Both the gaseous reactants are passed through humidifiers before feeding them to the cell. The flow rates for both hydrogen and oxygen gases are kept as 1.5 l/min using mass flow controllers (Aalborg Instruments and Controls, US). The humidifiers are kept 10 °C higher than the cell temperature. Measurements of cell potential as a function of current density are conducted galvanostatically using a LCN100-36 electronic load procured from Bitrode Corporation, US.

2.4.2. Cyclic voltammetry measurements

Cyclic voltammetry measurements are conducted at 25 °C to determine the electrochemical surface area using a potentiostat (Autolab-PGSTAT 30) with its leads for reference and counter electrodes connected to the cell anode, and its lead for working electrode connected to the cell cathode. During the experiment, gaseous hydrogen and gaseous nitrogen are fed to the anode and cathode, respectively. The voltammograms are recorded after a run time of ~1 h. During the first hour, the electrode is cycled, between 0 V and 1 V at a sweep rate of 50 mV/s to attain stable and reproducible voltammograms.

The electrochemical surface area (ESA) of Pt catalyst is estimated from the equation [23]:

$$ESA (cm2/gPt) = \frac{Q_{\rm H} (\mu C/cm^2)}{210 \,\mu C/cm^2 \times \text{electrode loading (gPt/cm^2)}}$$
(1)

where $Q_{\rm H}$ represents the charge of hydrogen desorption and 210 μ C/cm² is the charge required to oxidize a monolayer of H₂ on smooth platinum surface.

2.4.3. Characterization of the modified platinum catalyst

Characterization of catalysts is carried out using Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer Spectrometer), powder X-ray diffraction (X-ray diffractometer, Philips PanAnalytical), and X-ray photoelectron spectroscopy (X-ray Photoelectron Spectrometer, VG Scientific), in conjunction with pH measurements. FTIR and powder XRD provided information about surface functionality and particle size of platinum in the catalysts, respectively.

X-ray photoelectron spectra (XPS) for both modified and unmodified Pt/C were recorded on an ESCA Mark II Spectrometer (VG Scientific, England) using Al Kα radiation (1486.6 eV). Binding energies calibrated with respect to C(1s) at 284.6 eV are accurate within $\pm 0.2 \text{ eV}$ and there is no charging in any of the samples as they are conducting. For XPS analysis, the powder samples are made into pellets of 8 mm diameter and placed in an ultra high vacuum chamber at 10^{-9} Torr housing the analyzer. Prior to mounting the sample in the analyzing chamber, it is kept in the preparation chamber at 10^{-9} Torr for 5 h to expel any volatile species present on the catalyst. The experimental data are curve fitted with Gaussian peaks after subtracting a linear background. The spin-orbit splitting and the doublet intensities are fixed as described in the literature [24]. Binding energies for Pt (4f), S(2p), O(1s) and C(1s) are assigned with respect to Au $(4f_{7/2})$ at 83.9 eV.

The point-of-zero-charge (PZC) measurements are carried out for both modified and unmodified catalysts with pH adjusted deionised water. The pH is adjusted using different normality's of HCl and NaOH. The PZC is measured using pH meter (Elico-127L) adopting the procedure described elsewhere [25]. Before measuring PZC, both the modified and unmodified catalysts are washed three times with hot distilled water followed by drying in an air oven at 80 °C for 2 h. The pH of adjusted deionised water is referred to as the initial pH. Finally, the calculated amounts of supported catalysts (modified and unmodified) are separately



Fig. 1. FTIR spectra for (a) unmodified and (b) modified catalysts.

added to sample bottles containing deionised water at different pH values followed by sonication for 1 h. The pH is measured and recorded as the final pH.

3. Results and discussion

FTIR spectra for modified and unmodified catalysts are shown in Fig. 1. The spectrum for unmodified catalyst shows an intense band at 1590 cm^{-1} and a broad weak-band between 3200 cm^{-1} and 3500 cm^{-1} that could be attributed to stretching vibration of C=C and –OH group present onto the carbon support, respectively. The modified catalyst shows a broad intense-band in the region $3200-3500 \text{ cm}^{-1}$, which is attributed to –OH group attached to sulfur in the sulfonic acid group. The strong bands around 1700 cm^{-1} , 1090 cm^{-1} and a weak band near 1385 cm^{-1} are attributed to the stretching mode of sulfite group. These observations confirm that the phenyl-sulfonic acid groups are anchored to the carbon support and are akin to those reported by Peng et al. [14].

Powder X-ray diffraction (XRD) patterns both for modified and unmodified catalysts are shown in Fig. 2. The diffraction peak at $2\theta \approx 25^{\circ}$ in all XRD patterns is due to the (002) plane of the hexagonal structure of Vulcan-XC72R carbon, while the



Fig. 2. Powder X-ray diffraction (XRD) patterns for (a) unmodified and (b) modified catalysts.



Fig. 3. X-ray photoelectron spectra for Pt (4f) region in unmodified and modified catalysts.

peaks at ca. 40° , 47° and 68° are due to Pt (1 1 1), Pt (200) and Pt (220) face-centered cubic phases, respectively. The average particle diameter for the platinum particles is estimated as 4.2 nm from the broadening of the Pt (1 1 1) peak both for modified and unmodified catalysts, which indicates that the modification procedure has little effect both on the particle size and the powder XRD pattern. Notably, the particle size of platinum is smaller than the pores of carbon support. Accordingly, the presence of Pt particles inside the pores of carbon support is inevitable.

X-ray photoelectron spectra (XPS) for both modified (7.5 w/o phenyl-sulfonic acid loaded catalyst) and unmodified catalyst overarching the Pt (4f) region are shown in Fig. 3. For the unmodified catalyst, the binding energies of Pt $(4f_{7/2, 5/2})$ are observed at 71.2 and 74.4 eV, respectively. These binding energies correspond to Pt⁰ state. There is no oxidized Pt component in the 4f peaks as can be seen from the neat fitting of $4f_{7/2}$, 5/2 peaks. However, the phenyl-sulfonic acid anchored catalyst shows Pt (4f) peaks shifted to lower binding energy as compared to Pt^0 peaks. Accordingly, Pt (4f) peaks were resolved into two sets of spin-orbit doublets. Indeed significant peaks are observed due to $Pt^{\delta-}(4f_{7/2,5/2})$ at 70.5 and 73.9 eV, and $Pt^{0}(4f_{7/2,5/2})$ at 71.1 and 74.4 eV, respectively. It is noteworthy that formation of $Ag^{\delta-}$ and Au^{δ -} is reportedly known [26]. Concomitantly, the appearance of a small peak in Fig. 4 at a binding energy of 163.7 eV for S_{2p} can be accounted for S in 4+ state. The appearance of this peak for phenyl sulfonic acid anchored catalyst could be due to the oxidation of S^{2-} present in the carbon support. However, the peaks due to S^{2-} , which would normally appear at 162 eV could not be observed for unmodified catalyst due to low sulfur (bulk 0.3 wt.%), as it is beyond the detection limit of XPS [27]. Interestingly, S(2p) core level peak in Fig. 4 observed at a binding energy of 168.1 eV corresponds to -HSO₃ group with sulfur is in +6 state [28].

The change in the valance states of sulfur present on the carbon support of the catalyst and platinum after anchoring phenyl-sulfonic acid can also be visualized in the light of the PZC data for modified (5 w/o sulfonic acid) and unmodified catalysts shown in Fig. 5. The data confirm the anchoring of phenyl-sulfonic acid as the PZC value is reduced from 5.65 for



Fig. 4. X-ray photoelectron spectra for S (2p) region in unmodified and modified catalysts.

unmodified catalyst to 1.66 for the modified catalyst. This also suggests that the modified catalyst is more acidic than unmodified catalyst. These studies clearly suggest the phenyl-sulfonic acid groups to be anchored to the carbon support.

A larger reduction in PZC value for the modified catalyst in relation to the unmodified catalyst with reference to Vulcan XC-72R shows that the anchoring of phenyl-sulfonic acid groups strongly influences the charge density on the carbon to which the former is attached. This may influence the oxidation state of sulfur present in Vulcan-XC72R carbon. It is known that platinum is anchored to the carbon through sulfur and hence the change in oxidation state of sulfur is expected to influence the oxidation state of platinum [13,29].

The enhanced catalytic nature of the modified catalyst is further evaluated through cyclic voltammetry and polarization studies. Cyclic voltammetry (CV) studies are carried out to quantify the variation of electrochemical surface area (ESA) and percentage of platinum utilization with varying phenyl-sulfonic acid loading. The typical cyclic voltammogram is shown in Fig. 6. The peak between 0.0 V and 0.4 V provides the information on the hydrogen adsorption/desorption. The coulombic charge for oxidation of hydrogen, i.e. the area under the anodic peak minus the double-layer charge, increases with increased



Fig. 5. The point of zero charge (PZC) for unmodified and modified catalysts.



Fig. 6. Cyclic voltammograms for modified catalyst with varying phenylsulfonic acid loading (in w/o) onto the Pt/C (25 cm^2 single cell at $25 \degree \text{C}$; N₂ and H₂ streams at cathode and anode, respectively; scan rate = 50 mV/s).

Table 1

Hydrogen adsorption charge and electrochemical surface area of Pt with different w/o of phenyl sulfonic acid group anchored onto the catalyst-carbon support

w/o of phenyl sulfonic acid anchored on to Pt/C	$Q_{\rm H}~({\rm mC})$	Electrochemical surface area (ESA) (m ² /g of Pt)	
0	73.77	70.2	
2.5	99.35	94.62	
5	107.27	102.81	
7.5	95.45	90.9	

 $Q_{\rm H}$: experimentally determined adsorbed hydrogen charge. ESA: electrochemically determined active surface area from $Q_{\rm H}$ (assuming 0.210 mC/cm² for $Q_{\rm H}$ on smooth platinum).

loading of phenyl-sulfonic acid groups and reaches a maximum value at 5 w/o and subsequently decreases as the sulfonic acid loading is increased.

The electrochemical surface area (ESA) and adsorbed hydrogen charge ($Q_{\rm H}$) are calculated from CV data and the results are presented in Table 1. An increase in platinum utilization is found after anchoring phenyl-sulfonic acid group onto the carbon support. This is due to the extension of three-phase boundary



Fig. 8. Performance curves for PEFC with modified catalyst.

in the catalyst layer, especially inside the carbon agglomerate through phenyl-sulfonic acid group. This is further illustrated by the modified schematic diagram of the internal structure for the catalyst layer due to Uchida et al. [9] (see Fig. 7). The optimum loading is found to be 5 w/o. However, further increase in phenyl sulfonic acid loading to 7.5 w/o decreases Pt utilization possibly due to the increased hydrophilic nature of the catalyst layer, which leads to flooding albeit the amelioration exhibited by negative charged platinum sites that help repelling water molecules.

The performance of the H_2/O_2 PEFCs employing modified catalyst with 0, 2.5, 5 and 7.5 w/o loadings of *p*-amino phenylsulfonic acid are evaluated from cell polarization (voltage versus current density) data presented in Fig. 8. It can be seen that the cell comprising modified catalyst performs better in relation to the cell comprising unmodified catalyst over the entire polarization range. The maximum power density of 0.63 W/cm² is achieved at 0.5 V with modified catalyst having 5 w/o of phenylsulfonic acid, which is 40% higher than the unmodified catalyst (0.45 W/cm² at 0.5 V). However, the PEFC comprising electrodes with modified catalysts having 7.5 w/o phenyl-sulfonic acid loading exhibits a power density lower than the PEFCs



Fig. 7. Schematic illustration of electronic and ionic conduction paths in the catalyst layer for unmodified and modified catalysts.



Fig. 9. Effect of phenyl-sulfonic group loading (in w/o) on the current density at varying electrode potentials.

with modified catalysts having 2.5 and 5 w/o of *p*-amino phenyl-sulfonic acid loadings.

Higher amount of phenyl-sulfonic acid is expected to increase the utilization of platinum. However, the study indicates that the higher amount of phenyl-sulfonic acid shows lesser performance at high current densities. It could be due to reduced access of the reactant gas to the active sites because of flooding. Thus, platinum catalyst anchored with 5 w/o phenyl-sulfonic acid groups yields optimum PEFC performance with maximum permeability for reactants and catalyst utilization.

The cell potentials at varying load current densities as a function of the w/o of phenyl-sulfonic acid onto the carbon support are shown in Fig. 9. The data indicates that 5 w/o phenyl-sulfonic acid loaded catalyst shows superior performance at all load current densities. However, the catalyst loaded with 7.5 w/o phenyl-sulfonic acid shows sharp fall in voltage at 800 and 1200 mA/cm². These data confirm the optimum weight percentage of phenyl-sulfonic acid onto carbon-supported catalyst to be near 5 w/o.

The electrode kinetic parameters for the cells are summarized in Table 2. The cell potential (E) versus current density (i) data for varying amounts of sulfonic acid in the catalyst layer are analyzed by fitting the data to equation:

$$E = E_0 - b\log i - iR \tag{2}$$

where
$$E_0 = E_r + b \log i_0$$
 (3)

In Eq. (3), E_0 is the cell potential at a current density of 1 mA/cm², *b* is the Tafel slope, and *R* accounts for the linear

Table 2 Electrochemical kinetic parameters for PEFC with different w/o of phenyl sulfonic acid group anchored onto the carbon support

w/o of phenyl sulfonic acid anchored on to Pt/C	<i>E</i> ₀ (V)	$i_{0.9}^{a}$ (mA/cm ²)	b (V/decade)	$R(\Omega \mathrm{cm}^2)$
0	0.965	12.418	0.0731	0.2721
2.5	0.975	16.860	0.0626	0.2436
5	0.982	18.116	0.0563	0.2126
7.5	0.972	16.450	0.0686	0.2831

^a $i_{0.9}$ is the current density at the cell potential of 0.9 V.

variation of overpotential with load current density primarily due to ohmic resistance. The value of $i_{0.9}$ represents the current density at the cell potential of 0.9 V. The reason for presenting *i* at a particular cell potential and not i_0 is because even a slight variation in Tafel slope could cause anomalous variation in the values of i_0 [30,31].

As seen from the data in Table 2, the parameter *R* decreases with increasing phenyl-sulfonic acid content. The increase in resistance is significantly higher for unmodified catalyst than the modified catalyst. This is a clear manifestation of the ability of sulfonic acid groups in the catalyst layer to reduce membrane electrode assembly resistance due to the increased three-phase boundary. Thus, phenyl-sulfonic acid groups facilitate proton conduction in the catalyst layer. However, the increase in phenyl-sulfonic acid loading to 7.5 w/o increases the resistance due to increased hydrophilic nature of the catalyst layer. The values of E_0 and $i_{0.9V}$ are in conformity with the increased phenyl-sulfonic acid loadings.

The Tafel slopes for polarization curves for PEFCs with modified catalyst are lower than their unmodified catalyst. This could be due to the increase in the three-phase boundary in the catalyst layer that improves the ion-conducting path in the catalyst layer in addition to the repulsion of nearby water molecules from Pt sites on acquiring a negative charge, which enhances the electrochemical performance of the cell.

4. Conclusions

It is suggested that anchoring the phenyl-sulphonic group on the carbon support of the platinum catalyst enhances the performance of PEFC. This is achieved by increasing the utilization of Pt by enhancing the three-phase boundary in the catalyst layer. An optimum loading of phenyl sulfonic acid (5 w/o) is required to improve the performance of the PEFC. XPS studies suggest that anchoring of phenyl-sulfonic acid groups modifies the oxidation state of Pt that results in improved oxygen reduction kinetics.

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