Synthesis, characterization and electrochemical studies of Pt-W/C catalyst for polymer electrolyte membrane fuel cells

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Abstract. Pt-W/C catalyst was synthesized by slow reduction of platinum and tungsten solutions in the desired ratio with subsequent deposition on the Vulcan carbon already added to the solution. Crystallite size of catalyst was about 9nm and its density, cell volume, d-spacing and lattice parameter were also calculated. EDX analysis of the catalyst was also done. Electrochemical surface area of the catalyst was determined by cyclic voltammetry (CV). CV of the catalyst was done both in acidic and basic media to find out the peak potential, peak current, specific activity and mass activity of the catalyst. Peak potential versus scan rate plots showed that the electro oxidation of methanol is an irreversible process. Tafel equation was used to plot polarization curves to find out the exchange current density. Higher values of exchange current indicate better catalysts. Specific activities of the catalyst were determined in acidic and basic media and it was found that the specific activity in basic media increased substantially as compared to acidic media. The specific activity in acidic media was 83 mA/mg pt whereas in basic media it was 137mA/mg pt which is a substantial increase. Heterogeneous rate constant in acidic media was $6.15 \times 10^{-6}$ cm/s and in basic media it was $4.92 \times 10^{-5}$ cm/s which is much higher in basic media. In this binary catalyst addition of tungsten has increased the catalytic activity but it is non-noble metal thus will decrease the cost. Stability studies of the catalyst were done upto fifty cycles both in acidic and basic media and was found quite stable in both the media.

1. Introduction
Increase in energy demand and environmental concerns require the development of clean energy sources for sustainable development. Fuel cells may meet all the above requirements and are being developed as one of the primary energy technologies of the future [1-2]. Low temperature fuel cells particularly polymer electrolyte membrane fuel cells are important for automotive industry. Important technical parameters required for the automotive industry have been met including membrane electrode assembly (MEA) and diffusion media optimization and development of platinum alloy cathode catalysts. Vulcan carbon (XC-72R, 30–60 nm) is a commonly used support that fulfills the requirements of having better dispersion ability, conductivity and adequate strength [3-4] besides being cheaper. Work on carbon supported bimetallic Pt-nanoalloys with different metals have been reported for methanol oxidation which exhibited better efficiency but durability did not improve much [5-6]. Catalyst durability is still a challenge. Corrosion of carbon supports is the major reason for catalyst degradation [7]. Considerable work has been done on the development of ceramic materials as supports for low temperature fuel cells [8]. However, there are other important factors for catalyst supports such as surface area, porosity, electrical conductivity, electrochemical stability and surface...
It is reported that stability of WC is higher than carbon [10] and addition of platinum to WC increases the activity of the catalyst significantly [11]. The main drawback of WC supports is their low surface area as compared to carbon [12]. In this study carbon tungsten composite was used as a support and platinum was deposited to prepare a nanocomposite catalyst. The synthesized catalyst was characterized using XRD, EDX and cyclic voltammetry.

2. Materials and Methods

2.1. Chemicals and equipment
Platinum(IV) chloride PtCl₄, from Johnson Mathey, UK, Sodium tungstate Na₂WO₄.2H₂O, Aldrich, Hydrazine hydrate N₂H₄.2H₂O, Aldrich, Sodium borohydride NaBH₄ from Merck, Vulcan carbon, (XC-72) Aldrich, Methanol Sigma-Aldrich, 2-Propanol Merck, Nafion® 117 solution Sigma-Aldrich, Hydrogen peroxide 35% Applied Chem, Hydrochloric acid Sigma-Aldrich, Sulphuric acid Fluka, Nitric acid 65% Merck, Potassium hydroxide from Fluka were used.

The XRD spectra were recorded on X-ray diffractometer model 3040/60 X’Pert PRO. The XRD analysis of the catalyst was carried out in powder form with scan rate of 0.04 and 2θ values ranged from 10-90°.

Cyclic voltammetric measurements were carried out using Eco Chemie Autolab PGSTAT 12 potentiostat/galvanostat Netherlands, with the electrochemical software package GPES 4.9.

2.2. Synthesis of catalyst
Vulcan carbon employed had the diameter in a range of 30-60 nm (45 nm from XRD). Vulcan carbon was taken in a round bottom flask to which 6 M HCl was added. The contents were refluxed and ultrasonicated for 4 hours at 60 °C using E-30H (240 watts) ultrasonicator from Elmasonic, Germany. The acid treated Vulcan carbon was filtered off and was vacuum-dried for 24 hours at 110 °C. Functionalization of the purified vulcan carbon was also done by ultrasonication method in 4:1 v/v mixture of 8 M HNO₃ and 35% H₂O₂.

Aqueous solutions of Na₂WO₄.2H₂O and PtCl₄ were added to Vulcan carbon and stirred for 30 minutes. The mixture became colourless from light brown indicating adsorption of metal ions on carbon. Freshly prepared solution of NaBH₄ in the solvent mixture was drop wise added into the above dispersion. 4 hours stirring resulted formation of black suspension which was filtered vacuum dried for 24 hours at 110 °C. Syntheses were carried out under argon atmosphere to avoid formation of metal oxides.

2.3. Electrochemical measurements
For the CV measurements, three-electrode system was employed throughout the electrochemical measurements. Graphite electrode of surface area 0.785 cm² was used as a working electrode. Graphite electrode (GE) polished with 1.0 μm alumina washed in ethanol and ultra-pure water ultrasonically to remove organic and inorganic impurities from the surface of electrode. Then, 10 mg catalyst and 0.5 mL of water were mixed ultrasonically for 30 min. in a test tube. 40 μL of the suspension was pipetted out and pasted over the tip of polished graphite electrode, dried in air. After the solvent evaporation, 10 μL binder (5% nafion solution) was spread over the tip of surface of GE. Again dried it in air.

3. Results and Discussions

3.1. X-ray diffraction analysis
Fig.1 reveals the XRD patterns of Vulcan carbon, Pt/C, Pt-W/C. The diffraction peak at 24–26° and 54.01° observed in all the XRD patterns of the carbon-supported catalysts is due to the (002)
Table 1. XRD parameters evaluated for bi-metallic catalyst

| Catalyst                | Position 20° | d-spacing /Å | Lattice parameter a /Å | Cell volume V / Å³ | Density ρX-ray/g.cm⁻³ | Ave. crystallite size D/nm |
|-------------------------|--------------|--------------|------------------------|--------------------|------------------------|---------------------------|
| Pt₀.₁₀-W₀.₀₅/C          | 39.57        | 2.2773       | 3.9443                 | 61.36              | 20.68                  | 8.93                      |
| PSP*                    | 39.67        | 2.27         | 3.917                  | 59.87              | 21.51                  | -----                     |

Figure 1. XRD spectrum for the catalyst and support.

and (004) planes of the hexagonal graphitic structure of Vulcan XC-72 carbon [13]. Four characteristic peaks corresponding to (111), (200), (220), and (311) planes of the fcc crystalline Pt are observed in XRD patterns [14-15]. Pt standard pattern (00-001-1190) is used as a reference in order to confirm nanoparticles (NPs) formation. The standard peak observed at 20 position 39.67° was due to Pt (111) plane of fcc crystalline structure. A significant shifting of peaks was observed from 39.67° to 39.57° in Pt-W/C which is due to alloy formation of Pt with W. No peak for W metals and their oxides were observed. W metal forms amorphous oxide which was not indicated by XRD [9-11]. It indicates that secondary metal forms single phase crystalline structure with Pt.

Table.1 shows different parameter evaluated from the XRD patterns of mixed structures of Pt-W/C. There is small decrease in X-ray density. However, lattice parameter and cell volume increased.

3.2. EDX analysis

Compositional analysis of the synthesized catalyst was done by EDX. Initially 10% platinum, 5% Tungsten and 85% functionalized Vulcan carbon were added. EDX results are given in Table-2. It shows that in the synthesized catalysts the values are nearly the same with some small losses.
Table 2. EDX Analysis of catalyst

| Catalyst | Pt  | Co  | W   | Mo  | C   | O   |
|----------|-----|-----|-----|-----|-----|-----|
|          | ±0.001 | ±0.001 | ±0.001 | ±0.001 | ±0.001 | ±0.001 |
| Pt-W/C   | 9.51 | ------ | 4.38 | ------ | 83.69 | 2.42 |

3.3. Electrochemical Studies

3.3.1. Electrochemical surface area

Electrochemical surface area ($S_{ESA}$) is usually proportional to catalytic activity. Electrochemical surface area ($S_{ESA}$) can be calculated from the amount of charge transfer ($Q_{cat}$) in hydrogen adsorption region by applying equation

$$S_{ESA} = \frac{Q_{cat}}{Q_{Pt} \cdot L}$$

(1)

Where, $Q_{cat}$ is charge transfer from catalyst in hydrogen adsorption region ($\mu C$), $Q_{Pt}$ is the charge transfer for monolayer hydrogen adsorption ($210 \mu C \cdot cm^{-2}$) and $L$ is the mass of Pt loading (mg).

Table 3. Electrochemical surface area from CV in 1M $H_2SO_4$

| Catalyst          | Mass of Pt /mg | $Q_{pt-H}/\mu C$ | $S_{ESA}/(cm^2.mg^{-1})$ | $S_{CSA}/(cm^2.mg^{-1})$ | Roughness factor(cm$^2$) |
|-------------------|----------------|------------------|---------------------------|---------------------------|--------------------------|
| Pt$_{0.10}$-W$_{0.05}$/C | 0.10           | 3270             | 156                       | 32.49                     | 19.83                    |

Values of $Q_{cat}$ and $S_{ESA}$ are directly proportional to electro catalytic activity and are given in Table.3 for Pt-W/C catalyst. Higher value of roughness factor shows more efficient catalyst which show high activity for methanol oxidation [16]. Table-3 clearly shows that the introduction of non-noble metals such as W to Pt catalyst may play an important role in proficiently improving the $S_{ESA}$, enhancing surface accessibility for hydrogen adsorption/desorption and affecting the electrochemical activity of bi- metallic catalysts [17].

3.3.2. Cyclic Voltammetry for methanol electro-oxidation

CV was performed for the study of methanol oxidation on the graphite electrode modified with synthesized catalyst in acidic medium. Amount of methanol oxidized and the peak heights.
Figure 2. Cyclic voltammogram in acidic media

Table 4. Activity parameters evaluated from CVs measured at scan rate 50 mVs$^{-1}$

| Catalyst          | Peak potential $E_p$/V | Peak current $I_p$/(mA) | Specific activity $j$/(mA.cm$^{-2}$) | Mass activity mA/mg-Pt |
|-------------------|------------------------|-------------------------|--------------------------------------|------------------------|
| Pt$_{0.10-W}$ 0.05 /C, Acid media | 0.723                  | 8.29                    | 10.56                                | 82.9                   |
| Pt$_{0.10-W}$ 0.05 /C, Basic media  | -0.241                 | 13.71                   | 17.45                                | 137                    |

Current obtained is proportional to the catalytic activity of the catalyst. Fig. 2 shows CVs measured in 1.0 M CH$_3$OH + 1.0 M H$_2$SO$_4$ at scan rate 50 mV.s$^{-1}$. In anodic sweep, the electro-oxidation of methanol gives a well-defined forward anodic peak, while in cathodic sweep the electro-oxidation of methanol begins again and gives a reverse anodic peak. The presence of only anodic peaks in both anodic and cathodic sweeps indicates that electro-oxidation of methanol is an irreversible process [18]. Electro catalytic activity of various synthesized catalysts for methanol oxidation was also determined in basic medium using 1.0 M KOH solution by evaluating peak current ($I_p$) through CVs. Fig.3 shows CVs measured in 1.0 M CH$_3$OH + 1.0 M KOH at scan rate 50mVs$^{-1}$ from -0.7 to 0.4V on catalysts. In anodic sweep, a well-defined and sharp forward anodic peak was observed near at -0.3V, while in cathodic sweep very small reverse anodic peak was observed of the methanol oxidation.

Table 4 compares the peak potential, peak current, specific activity and mass activity for the oxidation of methanol in acidic and basic media. Catalyst activity is better in both the media but it is much better in basic media.
3.3.3. Exchange current densities from the Tafel plots

Tafel equation was used for the determination of exchange current densities. Tafel equation can be written as [19].

\[
\Delta V_{\text{act}} = a + b \log i
\]  

Where 
\[a = -2.3 \left( \frac{RT}{\alpha F} \right) \log i_0\]
\[b = 2.3 \frac{RT}{\alpha F}\]

The value of \(i_0\) can be evaluated from the intercept of the \(\Delta V_{\text{act}}\) vs \(\log i\) plots.

Table-5 shows the values of exchange current density as measured both in acidic and basic media. Values of exchange current are nearly similar in both the media.

### Table 5. Polarization data evaluated from Tafel plots

| Catalyst            | Tafel’s slope “b” (V decade\(^{-1}\)) | \(\alpha_n\) | Intercept of \(E\) vs. \(\log i\) E + F | \(i_0\) mA cm\(^{-2}\) |
|---------------------|--------------------------------------|---------------|--------------------------------------|---------------------|
| Pt\(_{0.10}\)-W\(_{0.05}\)/C, acid media | 0.218                                | 0.27          | 1.064                                | 15.47               |
| Pt\(_{0.10}\)-W\(_{0.05}\)/C, Basic media | 0.2279                               | 0.26          | 0.1079                               | 16.21               |

3.3.4. Rate constant of methanol oxidation

Rate of an electrochemical process can be calculated using different methods. Heterogeneous rate constant (\(k_h\)) was determined using the Nicholson-Shain equation [20]:

\[
i_p = 0.227 nFAC_o k_h \exp[(\alpha_n F/RT)(E_p-E^0)]
\]  

where \(i_p\) is the peak current, \(n\) is the number of electrons transferred, \(A/cm^2\) is the area of the electrode, \(C_o/mol/cm^3\) is the bulk concentration of the reactant and \(k_S/cm^s\) is the standard heterogeneous rate constant, \(F\) and \(R\) are the Faraday and gas constants.

Using equation a graph is plotted between \(\ln(I_p)\) vs. \(E_p-E^0\) to get a straight line and from the value of slope, \(k_{het}\) was calculated. Rate constants were measured both in acidic and basic media and are given in Table-6. It can be seen that rate constants are better in basic media than in acidic media and are better by a factor of ten. Performance of the catalyst is better in basic media.
Table 6. Rate constants of CH₃OH oxidation

| Catalyst                        | Peak current $i_p$/mA | Rate constant $k_{het}$/cm.s⁻¹ |
|---------------------------------|------------------------|-------------------------------|
| Pt₀.₁₀-W₀.₀₅/C, acidic media    | 8.29                   | 6.15x10⁻⁶                    |
| Pt₀.₁₀-W₀.₀₅/C, basic media     | 13.71                  | 4.92x10⁻⁵                   |

3.3.5. Durability of the catalysts

Great focus has been paid to the durability of catalyst in order to commercialize it for fuel cells. Bifunctional mechanism, comprising the incorporation of non-noble metal to Pt-catalyst, improved the durability of catalysts. Fig.4. shows durability of the catalyst in terms of specific activity obtained at scan rate 50mV.s⁻¹ for fifty numbers of cycles in a single run both in acidic and basic media. After each cycle, the value of current decreased in acidic medium. CO formation at the catalyst surface is a big reason which decreased the catalytically active sites of catalyst. In basic media after each cycle, the value of SA increased because catalyst becomes more and more active and less poisoning occurs in basic medium.

4. Conclusions

Addition of tungsten increased catalytic activity of platinum. XRD showed some alloy formation between platinum and tungsten. Catalytic activity of the catalyst was evaluated both in acidic and basic media. Catalytic activity was evaluated using Peak current, specific activity and mass activity and it was found that catalyst is efficient in both the media and comparatively more efficient in basic media. Exchange current and rate constants for the oxidation of methanol were also calculated and it was found that the performance of the catalyst was better in basic media. Durability studies were also done of the catalyst for oxidation of methanol repeating for fifty cycles and again the performance of the catalyst was better in basic media but it was generally stable in both the media. It can be concluded that rate of corrosion of the catalyst decreased with the addition of tungsten in both the media but it was better in basic media.
5. References
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