TiO$_2$ and Al$_2$O$_3$ promoted Pt/C nanocomposites as low temperature fuel cell catalysts for electro oxidation of methanol in acidic media

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Abstract. Carbon corrosion and platinum dissolution are the two major catalyst layer degradation problems in polymer electrolyte membrane fuel cells (PEMFC). Ceramic addition can reduce the corrosion of carbon and increase the stability of catalysts. Pt/TiO$_2$, Pt/TiO$_2$-C, Pt/Al$_2$O$_3$ and Pt/Al$_2$O$_3$-C catalysts were synthesized and characterized. Electrochemical surface area of Pt/TiO$_2$-C and Pt/Al$_2$O$_3$-C nanocomposite catalysts was much higher than the Pt/TiO$_2$ and Pt/Al$_2$O$_3$ catalysts. Peak current, specific activity and mass activity of the catalysts was also determined by cyclic voltammetry and were much higher for the carbon nanocomposites. Exchange current densities were determined from Tafel plots. Heterogeneous rates of reaction of electro oxidation of methanol were determined for all the catalysts and were substantially higher for titania catalysts as compared to alumina added catalysts. Mass activity of Pt/TiO$_2$-C was much higher than mass activity of Pt/Al$_2$O$_3$-C. Stability studies showed that addition of ceramics have increased the catalytic activity and durability of the catalysts considerably.

1. Introduction
In the modern society there is enormous demand for clean energy [1]. Non-renewable energy sources like fossil fuels (e.g. coal, petroleum, natural gas) are not sustainable for long period of time but also cause undesired pollution [2]. In the search of clean and efficient energy sources, fuel cells are emerging as alternate power sources particularly for transport [3]. Mostly efficiency of fuel cells depends on catalysts. For application in fuel cells the catalysts usually comprise of metallic nano particles (NPs) dispersed on suitable nano-support [4]. Most commonly employed nano-material supports are various forms of carbon that include Vulcan carbon (XC-72R), graphite, carbon nanotubes, and carbon nanofibers [4, 5]. Major drawbacks of carbon supported catalysts are corrosion and electrochemical surface area loss. When carbon support degrades and catalyst particle size grows then electrochemical surface area and performance are reduced [6]. Poisoning of the catalyst by CO is another problem. Ceramic oxides are emerging as catalyst supports [7], are resistant to corrosion and help in removal of adsorbed intermediates during methanol oxidation. Among metal oxides, besides others, TiO$_2$ [8], ZrO$_2$ [9], Al$_2$O$_3$ [10] and WO$_3$ [11] have been successfully employed as support material.

In this work Pt/TiO$_2$, Pt/TiO$_2$-C, Pt/Al$_2$O$_3$ and Pt/Al$_2$O$_3$-C have been synthesized and characterized. Vulcan carbon was functionalized by oxidative treatment. Electrochemical surface area, specific catalytic activity, exchange current, rates of methanol oxidation and durability studies of the catalysts were done and are compared.
2. Material and Methods

2.1. Pretreatment of Vulcan carbon
The Vulcan carbon XC-72 employed had the specific surface area 254 m$^2$g$^{-1}$ and average particle size 30nm, respectively. Vulcan carbon was purified by refluxing with conc. HCl and ultra-sonification at 60 $^\circ$C. It was filtered, washed and dried at 110 $^\circ$C. Functionalization of the purified Vulcan carbon was done by ultra-sonication method in 4:1 v/v mixture of 8M HNO$_3$ and H$_2$O$_2$. Titania and Alumina of analytical grade were used as received.

2.2. Synthesis of Pt/Vulcan carbon
Pt/Vulcan carbon (10 wt% Pt) catalyst was synthesized using NaBH$_4$ as reducing agent by conventional reduction method under argon atmosphere at room temperature. In a three-neck round bottom flask, aqueous solution of PtCl$_4$ was added and stirred under argon atmosphere along with Vulcan carbon; the mixture became colorless from golden indicating adsorption of metal ions on the Vulcan carbon. NaBH$_4$ solution in the solvent mixture was drop wise added into the above dispersion. 4 hours stirring resulted formation of black suspension which was filtered and washed several times with de-ionized water till neutral pH of the filtrate. The residue was vacuum-dried for 24 hours at 110$^\circ$C.

2.3. Synthesis of Pt/TiO$_2$-C and Pt/Al$_2$O$_3$-C Nanocomposite
Pt/TiO$_2$-C Nano composite catalyst was prepared with two step–methods. In the first step TiO$_2$ and Vulcan carbon were added into water: 2-propanol (3:1 v/v) mixture (the solvent) and ultra sonicated for 1 hour. The black solid was filtered, washed with deionized water, and dried in vacuum oven for 24 hours at 110$^\circ$C. TiO$_2$-C is a required composite support. In second step (10 wt% Pt) was loaded on this TiO$_2$-C mixed/composite support by conventional co-reduction method in which NaBH$_4$ used as a reducing agent. The resulting black suspension of Pt/TiO$_2$-C was filtered and washed several times with de-ionized water till neutral pH of the filtrate. The residue was vacuum-dried for 24 hours at 110$^\circ$C. Pt/Al$_2$O$_3$-C nancomposite catalysts was also prepared by the same procedure. For the preparation of Pt/TiO$_2$ and Pt/Al$_2$O$_3$ catalysts no carbon was added and other procedure was the same.

2.4 Electrochemical measurements of catalysts
Autolab PGSTAT 12 Eco Chemie (Netherlands) equipped with three-electrode system was employed for electrochemical studies under argon atmosphere at ambient temperature. Graphite electrode having exposed polished tip of surface area 0.785 cm$^2$ served as working electrode. For uniform mounting on the electrode, 20 mg catalyst was ultrasonically dispersed in 1 mL of the aqueous 2-propanol in a test tube for 30 minutes and 60 µL of the resulting suspension was spread on the tip. After evaporation of the solvent, 10 µL Nafion solution (5%) was applied to the tip and finally dried in air. Nafion was used as an ion exchange binder. Cyclic voltammograms were measured in the potential range from -1.0 to +0.5 V vs. SCE in the aqueous medium containing 0.2 M CH$_3$OH (Sigma- Aldrich, 99.7%) and 0.5 M KOH (Fluka, 99%).

3. Results and Discussions

3.1. Electrochemical surface area of catalysts
All the catalysts exhibit the typical electrochemical characteristics of polycrystalline Pt, that is, the evolution of currents for hydrogen desorption in the forward sweep and for the reduction of surface oxide and hydrogen adsorption on the reverse sweep [12]. Fig.1.and Fig. 2. Shows the characteristic cyclic voltammograms (CVs) measured in 1M H$_2$SO$_4$ at scan rate (u) 50 mV.s$^{-1}$ from potential range -0.2 to 1.0V on Pt/TiO$_2$-C, Pt/TiO$_2$, Pt/Al$_2$O$_3$-C, Pt/Al$_2$O$_3$ and Pt/C catalysts.
Hydrogen was adsorbed in the cathodic direction and then oxidized in the anodic direction, and the catalyst modified electrode showed well-defined hydrogen adsorption–desorption region. In forward scans, desorption of hydrogen take place from -0.25 to 0V and in reverse scan, reduction of hydrogen take place from 0 to -0.25V which shows adsorption of hydrogen on the catalyst surface. In reverse scans, oxygen reduction peak was observed at 0.47–0.48V. The specific electrochemical surface area (ESA) of Pt (sometimes referred to as the real Pt catalyst surface area) was calculated by integrating the CV curves in the hydrogen adsorption region by assuming that the charge per real cm\(^2\) of Pt with monolayer adsorption of hydrogen is 210 µC/cm\(^2\) [13]. Electrochemical surface area (S\(_{ESA}\)) may be evaluated from CV by determining the amount of charge transfer (Q\(_{cat}\)) in hydrogen adsorption region by applying equation

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

Where Q\(_{cat}\) is the charge for hydrogen adsorption , Q\(_{Pt}\) is the charge for a monolayer adsorption of hydrogen on polycrystalline Pt, which is 210 C (cm\(^2\) Pt\(^{-1}\)). L is the mass of platinum loaded on the electrode. Values of Q\(_{cat}\) and S\(_{ESA}\) are directly proportional to electrocatalytic activity. Knowing the real surface area of the catalysts, one may calculate the roughness factor (RF) by taking the ratio of real surface area to usual geometric area (or apparent area) of an electrode. The comparison of data of real surface area and roughness factor of different catalysts is given in table.1. It can be seen that electrochemical surface area of the composite supports is much higher than the normal carbon support for both the catalysts. Among the two composite catalysts electrochemical surface area of titania is much higher than alumina which indicates that titania supports are better than alumina in acidic media.
Table 1. Electrochemical surface area from CVs in 1M H₂SO₄ on various catalysts

| Catalysts       | Mass, Pt/mg | Qₚ₋₅Η/ C | SESA/cm².mg⁻¹ | Roughness Factor |
|-----------------|-------------|-----------|----------------|-----------------|
| Pt/C            | 0.16        | 4460      | 132            | 27.10           |
| Pt/TiO₂         | 0.12        | 1080      | 32             | 6.551           |
| Pt/TiO₂-C       | 0.16        | 9480      | 282            | 57.50           |
| Pt/Al₂O₃        | 0.24        | 1030      | 30             | 6.25            |
| Pt/Al₂O₃-C      | 0.16        | 5330      | 159            | 32.339          |

3.2. Electrooxidation of methanol on catalysts.
Catalytic activities of the catalysts for methanol oxidation (MO) were studied in acidic medium using cyclic voltammetry. Fig. 3 and Fig. 4. show the corresponding voltammograms measured in 1 M H₂SO₄ having 1 M CH₃OH at scan rate (υ) of 50 mV/s⁻¹. In anodic sweep methanol oxidation gives a well defined forward anodic peak, while in cathodic sweep MO again gives a reverse anodic peak, which indicates that MO is irreversible process. Table.2 presents various parameters which were calculated directly related to the electro catalytic activity. The performance of Pt/TiO₂-C is demonstrated by its highest values of peak current (iₚ), specific activity (Iₛ) and mass activity (Iₘ).
### Table 2. Various parameters calculated from CVs (in 1M CH$_3$OH + 1M H$_2$SO$_4$) at 298 K.

| Catalysts | Peak potential $E_p$/V | Peak Current $I_p$/mA | Specific activity $I_s$/mA cm$^{-2}$ | Mass activity $I_m$/mA mg$^{-1}$ Pt | Rate Constant $k_{het}$/cm$^2$s$^{-1}$ $10^{-5}$ |
|-----------|------------------------|-----------------------|--------------------------------------|-------------------------------------|---------------------------------------------|
| Pt/C      | 0.670                  | 4.87                  | 6.20                                 | 30.4                                | 1.62                                        |
| Pt/TiO$_2$| 0.678                  | 0.11                  | 0.14                                 | 1.00                                | 1.14                                        |
| Pt/TiO$_2$-C | 0.690                | 11.0                  | 14.0                                 | 68.7                                | 7.31                                        |
| Pt/Al$_2$O$_3$| 0.685               | 0.17                  | 0.21                                 | 0.71                                | 0.72                                        |
| Pt/Al$_2$O$_3$-C | 0.692              | 6.20                  | 7.90                                 | 38.7                                | 2.33                                        |

3.3. Comparison of Polarization Curves.

A polarization curve is the most important characteristic of a fuel cell and its performance. Here the polarization curves have been used for Tafel plots. Current–potential data was obtained by analyzing the forward anodic peaks for methanol oxidation. Polarization curves for titania and alumina are given in figs.5 and fig.6.

![Figure 5](image1.png)

**Figure 5.** Polarization curves for MO on Pt/TiO$_2$-C, Pt/TiO$_2$ and Pt/C.

![Figure 6](image2.png)

**Figure 6.** Polarization curves for MO on Pt/Al$_2$O$_3$-C, Pt/Al$_2$O$_3$ and Pt/C.

Tafel equation can be written as [14].

$$\Delta V_{act} = a + b \log i$$

Where $a = -2.3 \ (RT/\alpha F) \log i_0$  \quad b = 2.3 \ RT/ \alpha F
If voltage-current relationship is plotted in a logarithmic scale, the main parameters, a, b, and i₀ are easily detected. The catalytic activities of catalysts can be evaluated by comparing the data of exchange current density i₀. The value of i₀ can be evaluated from the intercept of the ΔV vs log i plots [14]. The values of exchange current densities for the composite catalysts are compared in table 3. It can be seen that exchange current for the composite catalysts are much higher than the carbon support alone. Among the composites titania has much higher exchange current than others.

### Table 3

| Catalysts | Tafel’s slope “b” (V decade⁻¹) | an | Intercept of E vs Log i | i₀ (mA cm⁻²) |
|-----------|-------------------------------|----|------------------------|------------|
| Pt/C      | 0.178                         | 0.331 | 1.049                    | 5.65       |
| Pt/TiO₂-C | 0.334                         | 0.177 | 1.249                    | 18.7       |
| Pt/Al₂O₃-C | 0.281                        | 0.211 | 1.991                    | 12.2       |

### 3.4. Comparison of heterogeneous rate constants.

Heterogeneous rate constants (kₛ) for the MO at temperature T can be determined using the Nicholson-Shain equation:[15-17]

\[
i_p = 0.227 nFAC_o k_s \exp\left[(an_a F/RT)(E_p-E_o]\right] \tag{3}
\]

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. Reinmuth (18) showed that for an irreversible reaction, the current flowing at the root of the wave is independent of the rate of voltage scan. Thus above equation can be written as

\[
i_p = 0.227 nFAC_o k_s \exp\left[(an_a F/RT)(E_p-E_i]\right) \tag{4}
\]

where \(E_i\) is the potential at the root of the wave. A plot of ln (\(i_p\) ) vs (\(E_p-E_i\)) at different scan rates will give rate constant from the intercept and \(an_a\) from the slope. As \(an_a\) decreases the voltammogram will be more drawn out. The rate constants for oxidation of methanol were calculated for all the catalysts and are given in Table-2. It can be seen that rate constant for Pt/TiO₂-C catalyst is much higher than the others. The rate constant \(k_s/cm^s\) value of 7.31·10⁻⁵ at 298 K for Pt/TiO₂-C is respectively 6.5 and 4.5 times higher than those obtained for Pt/TiO₂ and Pt/C in acidic medium. While on the other hand Pt/Al₂O₃-C have rate constant 2.33·10⁻⁵ cm/s which is also higher than Pt/C catalysts which are normal commercial catalysts. Here, in Table-2 values of peak current (\(i_p\)) specific activity (\(I_s\)) and mass activity (\(I_m\)) are given for the catalysts Pt/TiO₂-C, Pt/Al₂O₃-C, Pt/TiO₂, Pt/Al₂O₃ and Pt/C. The comparison of all synthesized catalysts Table-2 corroborated that Pt/TiO₂-C catalyst showed 4.5 times better electrocatalytic activity than that of Pt/C, 6.4 times from Pt/TiO₂, 3.1 times from Pt/Al₂O₃-C and 10.1 times from Pt/Al₂O₃. From rate constants it is also shown that composite catalysts are much better than the commercial catalysts. It further shows that catalytic activity of Pt/TiO₂ is near to that of commercial type of catalysts. Thus ceramics alone can also be used as supports which will enormously increase the durability of the polymer electrolyte membrane fuel cells and these fuel cells can also be used for the production of hydrogen.
Figure 7. Catalyst durability plots showing specific activity (j) vs. number of cycles in a medium containing 1 M H₂SO₄ and 1 M CH₃OH (scan rate 50 mV s⁻¹).

3.5. Durability study of Catalysts.

Figure 7, shows catalyst durability plots when subjected to fifty cycles at scan rate of 50 mV s⁻¹. Promoted mechanisms (hydrogen and oxygen spill over effect) has been observed in case of ceramic based nanocomposites, in which CO ads on Pt sites can spill on neighbor ceramic (TiO₂ and Al₂O₃) particles adsorbing OH species. The rapid oxidation will form more free Pt sites covered by CO. So, durability depends on the mechanism of the MO occurring at the catalyst surface. Fig. 7 shows the durability of Pt/TiO₂-C, Pt/Al₂O₃-C and Pt/C catalysts in term of specific activity obtained for 1M CH₃OH + 1M H₂SO₄ at scan rate 50mV.s⁻¹ for fifty numbers of cycles in a single run. In all these catalysts peak current decreased for first ten cycles and then up to fifty cycles it stabilized for the composite catalysts and there was decrease for carbon supported catalyst. Although the Iₛ values increase for all the three catalysts, the plot for Pt/TiO₂-C not only lies much higher but it also becomes horizontal demonstrating a consistent efficiency with time. Decrease in the catalytic efficiency may be attributed to poisoning of the Pt active sites however, presence of TiO₂ and Al₂O₃ in support improved the efficiency and stability of the catalyst. The catalytic activity of carbon supported catalyst showed decrease with increasing the number of cycles, may be due to poisoning of active sites of the catalysts.

4. Conclusions

Ceramic-carbon supported composite fuel cell catalysts have been developed with enhanced catalytic activity. Titanium oxide and aluminum oxide inclusion in Carbon support improves the electrocatalytic activity and stability of the catalysts because metal oxide in supports exhibit a promising effect on metal and have role in removing poisoning intermediates like CO from the active sites of the catalyst. Durability study has shown that ceramic based composite catalysts are not only efficient but are also durable. Ceramic-based nanocomposites have higher electrochemical surface area and higher catalytic activity when evaluated for exchange current and rate of reaction in acidic medium. Pt/TiO₂-C showed higher performance than Pt/Al₂O₃-C, Pt/TiO₂, Pt/Al₂O₃ and Pt/C catalysts. Pt/TiO₂-C has maximum efficiency in acidic media. Pt/TiO₂ has better efficiency than Pt/C. Pt/TiO₂ has good efficiency and is a potential catalyst to replace the commercial carbon based catalysts which are...
suffering from corrosion and degradation problems. It can be concluded that the catalyst supports for metal catalyst have an important role in electrodes development for the low temperature fuel cells.

5. References

[1] Apergis, N.; Payne, J. M. Energy Economics. (2011).
[2] Munuswamy, S.; Nakamura, K.; Katta, A. Renew. Energy 36 (2011) 2978–2983.
[3] Haung, S.Y.; Ganesan, P.; Park, S.; Popov, P. N. J. Am. Chem. Soc. 131, 2009, 13898–13899.
[4] Kumar, S. S. M.; Hidyatai, N.; Herrero, J. S.; Irusta, S.; Scott, K. Int. J. Hydrogen Energy, 2011, 36, 5453–5465.
[5] Guo, D. -J.; Qiu, X. -P.; Chen, L. -Q.; Zhu, W. -T.; Carbon, 2009, 47, 1680–1685.
[6] Garzon, F.H., Davey, J.R., Borup, R.L. ECS Meeting Abstracts, Vol.MA, 2005-02,2223
[7] Antonili, E.; Gonzalez, E.R.J. Appl. Catalysis A, 2009, 365, 1–19.
[8] Haung, S. –Y.; Ganesan, P.; Popov, B. N.; J. Appl. Catal. B: Enviromental, 2011, 102 71–77.
[9] Djerad, S., Geiger, B., Schott, F.J.P., Kureti, S., Catal. Commun. 2009, 10, 1103–1106.
[10] Luo, M. F.; Lin, W.R.; Wen, W. H.; Chang, B.W. Surf. Sci. 2008, 602, 3258–3265.
[11] Antonili, E.; Gonzalez, E.R. J. Appl. Catal. B: Enviromental, 2010, 96, 245–266.
[12] Qian, Y.; Wen, W.; Andock, P.A.; Jiang, Z.; Hakim, N.; Saha, M.S.; Mkherjee S. J. Phys Chem C 2008, 112, 552-557.
[13] Yan, S., Zhang, S., Lin, Y., Liu, G. J. Phys. Chem. C 2011, 115, 6986–6993.
[14] Barbir, F. 2005, PEM Fuel Cells: Theory and Practice, Elsevier Academic Press, Amsterdam,
[15] Khan, A.S.A., Ahmed, R., Mirza, M.L., Turk. J. Chem. 2008, 32, 743–753.
[16] Nicholson, R.S., and Shain. I. Anal. Chem; 1964, 36, 70,
[17] Bard, A. J., Faulkner, L.R., 2001, Electrochemical methods, Fundamentals and applications, J. Wiley & Sons, New York, pp.231, 251.
[18] Reinmuth, W.H., Anal. Chem. 1960, 32, 1891.