

SYNOPSIS OF

**ELECTRO-CATALYTIC SUPPORTS FOR NOBLE METALS
FOR EXPLOITATION AS ELECTRODES FOR FUEL
CELLS**

*A THESIS
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INTRODUCTION

Since the last decade, fuel cells have been receiving increased attention due to the depletion of fossil fuels and rising environmental concerns. Fuel cells have been demonstrated as an interesting and a promising alternative to solve the problem of clean electric power generation with high efficiency. Among the different types of fuel cells, Direct Methanol Fuel Cells (DMFCs) are excellent power sources for portable applications owing to their high energy density, ease of handling liquid fuel, lower operating temperatures (60 – 100 °C) and quick start up (Hogarth et al., 1996, 2002, Ralph et al., 2002). Furthermore, methanol fuel cells seem to be highly promising for large-scale commercialization in contrast to hydrogen-fed cells in terms of transportation (McNicol et al., 1999). The limitation of methanol fuel cell system is due to low catalytic activity of the electrodes, especially the anodes. At present, there are no practical alternatives to Pt based catalysts. High noble metal loadings on the electrode and the use of perfluorosulfonic acid membranes are significantly contributing to the cost of the fuel cell devices (Hamnett et al., 1997, Wasmus et al., 1999)

MOTIVATION

An efficient way to decrease the loadings of precious platinum metal catalysts and higher utilization of Pt particles can be achieved by better dispersion on a suitable support (Watanabe et al., 1989, Matsumoto et al., 2004). In general, small particle size and high dispersion of platinum on the support result in higher electro-catalytic activity. Carbon materials possess suitable properties for designing of electrodes in electrochemical devices. Therefore, carbon is an ideal material for supporting nano-sized metallic particles in the electrodes for fuel cell applications. The conventional support namely carbon black is used for the dispersion of Pt particles (Uchida et al., 1995). New novel carbon support materials such as graphite nanofibers (GNF) (Bessel et al., 2001, Steigerwalt et al., 2001), carbon nanotubes (CNT) (Li et al., 2003, Han et al., 2004, Wang et al., 2004), carbon nanohorns (Yoshitake et al., 2002) and carbon nanocoils (Hyeon et al 2004), provide alternate candidates of carbon support for fuel cell applications. The most efficient utilization of any supported

catalyst depends on the percentage exposed or the dispersion of the active component on the surface of the carrier material. Among the various factors that influence the dispersion of active component, the nature of the support and the extent of the active component loading, are of considerable importance.

OBJECTIVE AND SCOPE OF THE PRESENT WORK

Development of anode electro-catalyst with maximum utilization of Pt on different type of nanostructured support for methanol oxidation is another area of research interest in this study. The work presented here is a compilation of different type of nanostructured electrodes as supports for methanol oxidation in direct methanol fuel cells.

The objectives of the present work are

1. To develop unconventional supports for platinum catalysts for methanol oxidation and compare the methanol oxidation activity of nanostructured supported catalysts with that of the commercially available Vulcan XC-72 based catalysts.
2. Synthesis of Nitrogen containing carbon nanotube supported Pt electrodes for methanol oxidation.
3. Synthesis of TiO₂ nanotube supported Pt electrodes for methanol oxidation.
4. synthesis of Pt/WO₃ nanorods as anode electro-catalyst for methanol oxidation in DMFC application
5. Synthesis of new conducting polymer nanotubes and subsequent deposition of Pt.
6. Synthesis of Pt supported on PEDOT-V₂O₅ polymer composite electrodes for for methanol oxidation.
7. Physio-chemical characterization of the synthesized materials
8. Evaluation of performance of electrooxidation of methanol in acid medium on the above synthesized materials.

DESCRIPTION OF THE RESEARCH WORK

The research work will be described in five sections

Section I

Role of Nitrogen functionality in the carbon nanotube supported Electrodes for methanol oxidation

Carbon has the essential properties of electronic conductivity, corrosion resistance, surface properties and low cost as required for the commercialization of fuel cells.

Carbon with nitrogen, sulphur and phosphorus functionalities promotes the formation of Pt particulates with reduced dimensions relative to unfunctionalised carbon. Electrocatalysts prepared with nitrogen-functionalised carbon showed the highest activity towards methanol oxidation (Roy et al., 1996). While sulphur-functionalised electrode showed the lowest activity towards methanol oxidation, suggesting the existence of specific interaction between Pt and sulphur on the carbon support which inhibited the rate of the reaction (Swider et al., 2000). Nitrogen functionalisation was accompanied by an increase in basicity of the carbon support, while sulphur functionalisation resulted in increase of acidity. The presence of nitrogen functional groups in the carbon framework has also a substantial effect on the catalytic activity in direct methanol fuel cells (Shukla et al., 1994, Roy et al., 1997).

Nitrogen containing carbon nanotubes were synthesized by impregnating nitrogen-containing polymers inside the alumina membrane template and subsequent carbonization of the polymer. The polymers used are Polyvinylpyrrolidone (PVP), polypyrrole (PPY) and polyvinylimidazole (PVI) are impregnated or polymerized on the alumina template and carbonized in the electric furnace at 900 °C under Ar atmosphere. The resulting carbon–alumina composite was immersed in 48% HF at room temperature for 24 h to remove the alumina template. The carbon nanotubules obtained as an insoluble fraction were washed with distilled water to remove the residual HF and then dried in air at 120 °C. SEM, TEM, AFM have characterized the nanotubes.

Loading of Pt catalyst on the carbon nanotubes and nitrogen containing carbon nanotubes

Platinum nanoclusters were loaded inside both the CNT and the N-CNT as follows; the C/alumina composite obtained (before the dissolution of template membrane) was immersed in 73 mM H_2PtCl_6 (aq) for 12 h. After immersion, the membrane was dried in air and the ions were reduced to the corresponding metal by 3 h of exposure to flowing H_2 gas at 823 K. The underlying alumina was then dissolved by

immersing the composite in 48 % HF for 24 h. The membrane was then removed from the HF solution and treated in the same way as for the unloaded CNT to remove the residual HF. This procedure resulted in the formation of Pt nanocluster loaded CNT and N-CNT. The complete removal of fluorine and aluminum is confirmed by EDX analysis.

Electrocatalytic activity of the catalyst

Electrode	Nitrogen content	Activity Ip (mA/cm²)
Pt	-	0.076
GC/ 20% Pt/C (E-TEK)Naf	-	1.3
GC/CNT _{PPP} -Pt -Naf	0.0	12.4
GC/CNT _{PVP} -Pt -Naf	6.63	16.2
GC/CNT _{PPY} -Pt -Naf	10.5	21.4
GC/CNT _{PVI} -Pt -Naf	16.7	18.6

The electrocatalytic activity of methanol oxidation of the Pt/N-CNT electrodes has been evaluated, which is then compared with that of the Pt/CNT electrode and the conventional carbon supported platinum (E-TEK, Pt 20 wt%) electrode. The N-CNT electrode with optimum nitrogen content 10.5 % shows higher electrocatalytic activity is due to higher dispersion and a good interaction between the support and the Pt particles.

Section II

Preparation and electro-catalytic studies on Novel Pt supported TiO₂ Nanotube Electro catalyst for methanol oxidation

Titanium oxide (TiO₂) and materials derived from TiO₂ are widely investigated for applications in photovoltaic cells, batteries, separators, sensing devices, optical emissions, photonic crystals, catalysis and photocatalysis, selective adsorption, ion exchange, ultraviolet blockers, smart surface coatings, and as functional filling materials in textile, paints, paper, and cosmetics and also electrode material for methanol oxidation (Avalle et al., 1992, Hayden et al., 2001, Macak et al., 2005, Hepel et al., 2006).

Recently, TiO₂-based nanotubes began to attract wide attention because of their potential in many areas such as highly efficient photocatalysis and photovoltaic cells. Mainly, two approaches were reported for preparing titania nanotubes in

powdery forms, one using a templating synthesis and the other using a hydrothermal reaction.

Titanium isopropoxide (5 mL) was added to 25 mL of 2-propanol. The solution was stirred for 3 h at room temperature (298 K). The alumina template membrane was dipped into this solution for 1 min. After removal from the solution, vacuum (vacuum pump) was applied to the bottom of the membrane until the entire volume of the solution was pulled through the membrane and it is slowly hydrolyzed by water vapour of solution of 20 mL of 1 M HCl and 120 mL of deionised water. The membrane was air-dried for 60 min at room temperature, and then placed in a furnace (in air) with a temperature ramp of 2 C h⁻¹ to 873 K for 2 h. The Anatase form of TiO₂ nanotube formed on the pores of the alumina template was immersed in 73 mM H₂PtCl₆ (aq) for 12 h. After immersion the membrane was dried in air and the ions were reduced to the corresponding metal(s) by a 3 h exposure to flowing H₂ gas at 823 K. The underlying alumina was then dissolved by immersing the composite in 3 M NaOH. The membrane was removed from the NaOH solution and treated in the same way as for unloaded CNT to remove residual HF. This procedure resulted in Pt nanocluster loaded TiO₂ Nanotube.

Electrochemical parameters for methanol oxidation on the various electrodes		
Electrocatalyst	Anodic scan peak potential (V) vs Ag/AgCl	Anodic peak current density (mA/ cm²)
Bulk Pt	0.640	0.16
20 % Pt/C	0.762	1.3
Pt/TiO ₂ nanotube	0.680	13.2

This synthesized TiO₂ nanotube by template synthesis was used for supporting Pt nanoparticles has been deposited using electroless deposition and the electro catalyst has been evaluated for methanol oxidation and shows good catalytic activity. The results showed that the high electro-catalytic activity for methanol oxidation is due to the high dispersion of Pt particles on TiO₂ nanotube electrode. The good stabilities can be attributed to the synergistic effect between Pt and TiO₂, avoiding the electrodes being poisoned.

Section III

Higher Activity of Pt Supported on WO₃ Nanorods – Alternate Anodes for Methanol Oxidation in Direct methanol fuel cell

Tungsten oxide is a well-known multifunctional material, especially for fuel cell applications (Hobbs et al, 1969). We have utilized tungsten oxide nanorods as support for the following reasons. Platinum catalysts supported on tungsten oxide have been extensively studied as active catalysts for the electro-oxidation of methanol (Shen et al, 1994). Tungsten oxide can form hydrogen bronze (H_xWO_3) that effectively facilitates the dehydrogenation of methanol (Kulesza et al, 1994) though these catalysts exhibit high performance, tungsten oxide undergoes dissolution in acid media and this reduces the electrocatalytic activity. The stability of tungsten oxide in acid media can be improved by suitably adjusting the conditions of its preparation

Application of the tungsten oxide matrix should increase the electrochemically active surface area and facilitate charge (electron, proton) distribution (Yang et al, 2004). Although to the lower extent that in the case of ruthenium species, the $-OH_{ads}$ groups existing on tungsten oxide surface may induce oxidation of the poisoning CO intermediate (Shen et al, 1994). The present study aims at fabrication of multi-component electrocatalytic system with optimized reactivity towards electrooxidation of methanol. On the whole, the system is multifunctional in terms of promoting oxidation of methanol.

Synthesis of WO_3 nanorods

10 g of Phosphotungstic acid ($H_3PW_{12}O_{40}$) was stirred in a 30 ml of methanol solution. The resulting colloidal suspension was infiltrated into the membrane under vacuum by wetting method. The same procedure was repeated 1 to 8 times. The upper surface of the membrane was then polished gently by sand paper (2500 grit) and dried at $95^{\circ}C$ for 1 h. The formation of WO_3 nanorods inside alumina template (WO_3/AAO) was further achieved by programmed temperature thermal decomposition from 95 to $500^{\circ}C$ at $10^{\circ}C\ min^{-1}$ and finally calcinated at $873\ K$ for 3 h in air. The removal of the AAO template was performed by dissolving alumina template in 10 % (v/v) HF. The WO_3 nanorods product was washed with a copious amount of deionized water, to remove the residual HF and dried at $393\ K$.

Synthesis of Pt/ WO_3 nanorods composites

Platinum nanoclusters were loaded on the WO_3 nanorods by conventional impregnation methods. Platinum was loaded on the nanorods as follows: 5 ml of 73mM aqueous hexachloroplatinic acid (H_2PtCl_6) was mixed with 100 mg of WO_3

nanorods by stirring at room temperature. The mixture was then evaporated to dryness and the resulting material was then reduced in hydrogen atmosphere at 623 K for 3h to give Pt/WO₃ nanorods.

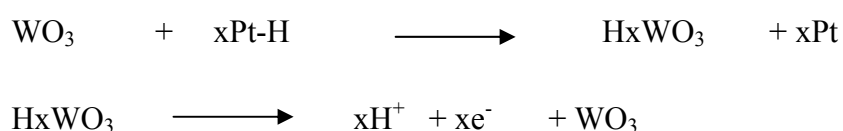
Electrocatalytic activity of the catalyst

The electrochemical activity of platinum loaded WO₃ nanorods for methanol oxidation was studied using cyclic voltammetry in the presence of 1M H₂SO₄ and 1M CH₃OH. Like Ru, WO₃ also has no activity for methanol oxidation in acid solution. The unsupported WO₃ nanorods showed no activity towards methanol oxidation.

Table 1. Electro-catalytic activity of Pt/WO₃ nanorods and Pt/C for methanol oxidation

Electrocatalyst	Pt loading μg/cm²	Specific activity mA/cm²
Pt/C	20	29.5
Pt/WO ₃ nanorods	20	62.0

The advantages of using Pt/WO₃ electrode are (1) keeping the Pt site clean for chemisorption of methanol by the formation and oxidation of hydrogen tungsten bronzes during dehydrogenation of methanol on the surface of Pt/WO₃ electrode.



And (2) oxidizing the poisons such as CO, since water adsorbed on WO₃ surface can interact with CO adsorbed on Pt at the neighbouring site. Such bronzes show better catalytic activity than Pt-Ru based electrocatalysts. Also the oxophilic nature of WO₃ is beneficial to producing hydroxyl groups on the catalyst surface, which promotes the oxidation of adsorbed CO.

Section IV

Template Synthesis and Electro-catalytic activity of Conducting Nitrogen Functionalized Polymer Nanotube Supports

Among many conducting and electroactive polymers, Poly (o-phenylenediamine) (POPD) is of great interest regarding its potential use in various fields of technology. Two interesting properties of POPD, different from those, characteristic for usual

conducting polymers like Polyaniline (PANI) or Polypyrrole (PPY) make it promising for applications in electrochemical and bioelectrochemical sensors. One of these properties relate to an unusual dependence of the electric conductivity on the redox state of this polymer. As opposed to PANI or PPY, POPD shows the conductivity in its reduced state, whereas its oxidized state is insulating. This determines the electrochemical properties of POPD, since many electrode redox processes of solution species have been shown to take place within a relatively narrow potential window, corresponding to the reduced (conducting) form of this polymer. Within this potential window, electrocatalytic oxidation of some species proceed, making it possible to use POPD for electrocatalytic applications, like e.g. the electro oxidation of coenzyme NADH, electro oxidation of methanol (Golabi et al 2002, Golabi et al 2003, and oxygen reduction (Ohsaka et al., 1998, Li et al 1998, Premkumar et al., 1996)

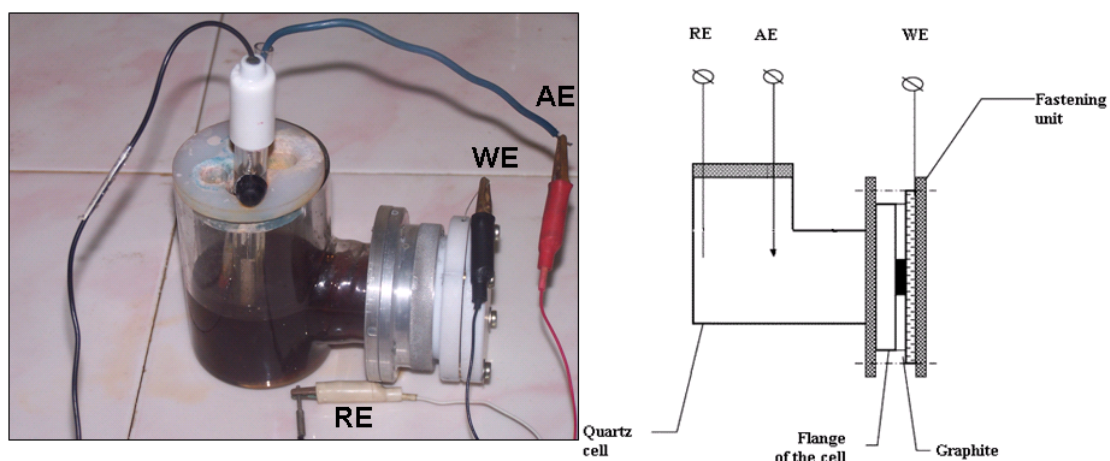


Figure 1 Schematic view of an electrochemical cell for the formation of nanostructured materials. RE, reference electrode; AE, auxiliary electrode; WE, working electrode (template membrane with a deposited Nafion contact layer).

The present work was carried out in aqueous solutions. Purified water obtained by passing distilled water through a milli Q (Millipore) water purification system was used as solvent. O-Phenylenediamine (o-PD) was purchased from Aldrich. All experiments were carried out in a conventional one-compartment cell with a Pt counter electrode and a saturated calomel reference electrode, at room temperature. First the graphite electrode is coated with Nafion solution. The Nafion is not only acts as binder but provides both ionic and electronic contact and favors

proton transport and the membrane is hot pressed with the Nafion coated graphite. Second the graphite electrode was used as current collector and contact with the template membrane. The Membrane together with the current collector was fixed between two Teflon rings. The area of the membrane contacted to the electrode was ca. 1 cm². The solution was de-aerated by bubbling dry Nitrogen gas for 5 min before electrochemical polymerization. The electro polymerization of PPD was carried out with a BAS 100B Electrochemical Workstation (Bioanalytical Systems Inc., West Lafayette, IN). The poly o-phenylenediamine tubules were grown potentiodynamically -0.2 V to 1.2 V containing 5 mM O-phenylenediamine + 0.5 M H₂SO₄. Deposition of platinum particles into the Popd nanotube by electro reduction of chloroplatinic acid (0.01 M) in 0.5 M sulfuric acid. Each electro reduction step involved ten potential cycles in the range from 0.8 to -0.3 V (scan rate =50 mV s⁻¹). Under these conditions, the amount of loaded platinum particles was determined as 0.1 mg cm⁻² from the charge passed during the loading step.

Evaluation of methanol oxidation activity of GR/Naf/PoPD Temp -Pt nanotubule and GR/Naf/PoPD-Pt electrodes

S. No	Electrode	Onset Potential (V)	Activity*			
			Forward sweep		Reverse sweep	
			I (mA cm ⁻²)	E (mA cm ⁻²)	I (mA cm ⁻²)	E (mA cm ⁻²)
1	GR/Naf/PoPD _{Temp} - Pt	+0.37	84	0.82	--	---
2	GR/Naf/PoPD _{Conv} - Pt	+0.2	13.3	0.70	6.	0.45

The electrochemical properties of the nanotubules electrode were compared with those of the conventionally synthesized poly (o-phenylenediamine) on graphite, using cyclic voltammetry. The Pt incorporated poly (o-phenylenediamine) nanotube electrode exhibited excellent catalytic activity and stability compared to the 20 wt % Pt supported on the Vulcan XC 72R carbon and Pt supported on the conventional poly (o-phenylenediamine) electrode. The nanotubules electrode showed excellent electro-catalytic activity and stability for electro- oxidation of methanol.

Section V

Synthesis of Pt supported on poly (3, 4-ethylenedioxythiophene) PEDOT/V₂O₅ Nanocomposites and their application in methanol oxidation

There has been a great deal of interest in recent years on the preparation of conducting polymer based nanocomposite for fuel cell applications. In particular, a comparison of the application of either conjugated polymers or transition metal oxides individually with the nanocomposite as electrodes for methanol oxidation in direct methanol fuel cells (Rajesh et al., 2005). At this juncture, recent advances have shown that electronic conducting polymers such as polypyrrole, polyaniline, polythiophene and poly(3,4-ethylenedioxythiophene) can serve as porous supports to disperse the platinum particles and the resulted composites have excellent properties. Polyaniline (PANI) has been applied extensively to support platinum catalysts (Mark et al., 1999, Chung et al., 2006).

The use of carbon and possibly other electronic conductors in the catalyst layer has been proposed for increasing the utilization of the catalyst by increasing electrical connectivity between catalyst particles. However, the relatively low density of carbon results in thick catalyst layers that impede the mass transport of methanol to the catalytic sites. Furthermore, the polymer-electrolyte membrane material is acidic and most metals are not chemically stable in contact with it. Finally, a material that conducts electrons (but not protons) does not contribute to the needed transport of protons produced in the electro-oxidation reaction.

An alternative is to develop a catalyst support that is permeable to gases and water, while conducting both protons and electrons efficiently. Such a material could replace both carbon and Nafion in the catalyst layer and should provide enhanced performance. Elsewhere we have described the use of polypyrrole/poly (styrene-4-sulfonate) (PPY/PSS) in such a role. However, because of the poor stability of the polypyrrole we were unable to deposit appropriately small Pt particles without appreciable losses of electronic conductivity. As a consequence, the performances of the PPY/PSS supported catalysts for oxygen reduction in gas diffusion electrodes were only modest (Qi et al., 1998)

We have here reported on the synthesis, and electrochemical studies, of a more stable conducting Poly (3, 4-ethylenedioxythiophene)/ (PEDOT/ V_2O_5) nanocomposites. This material was shown to have an appropriately high surface area for use as a catalyst support and to exhibit high electron and proton conductivities. Furthermore, since V_2O_5 is a strong oxidant. V_2O_5 acts as a good oxidation catalyst.

As it shown here, it can be catalyzed with nanometer-scale Pt particles to produce excellent fuel cell catalysts.

Synthesis of poly (3, 4-ethylenedioxythiophene)/ V₂O₅ nanocomposites

Vanadium oxide (V₂O₅) powder (1 g, or 5.5×10^{-3} mol) is mixed with 100 ml aqueous solution of hydrogen peroxide (10%). As H₂O₂ decomposes, oxygen gas evolves and voluminous bright yellow foam forms spontaneously. Vanadium oxide reacts with hydrogen peroxide to give V₂O₅.*n*H₂O gels (Chandrappa et al., 2002) that have a layered structure composed of negatively charged vanadium oxide ribbons. These gels can intercalate a wide variety of inorganic and organic species, such as EDOT. In the foaming process described here, gelation and intercalation both occur when the EDOT and hydrogen peroxide solutions are added to vanadium oxide powder. The intercalation of EDOT between the V₂O₅ layers creates a pasty solid, while the hydrogen peroxide decomposes spontaneously in the presence of vanadium oxide. Large pores are formed by oxygen gas released through the viscous gel in the presence of EDOT: as they escape, the oxygen bubbles cause the formation of voluminous polygonal foam, without destroying the crystalline structure of the oxide network of surfactant molecules intercalated between the layers of vanadium oxide.

Synthesis of Pt supported PEDOT/ V₂O₅ nanocomposites

The nanocomposites powder (ca. 100 mg) was ground gently with a mortar and pestle then suspended in about 20 mL H₂O. H₂PtCl₆ hydrate (Aldrich) for deposition of Pt was then added in an amount slightly greater than the desired loading. The suspension was stirred at ca. 80⁰C for 30 min to allow dispersion and equilibration, then ca. 25 molar excess of aqueous formaldehyde (BDH, 37%) was added followed by heating at reflux for 1 h. The catalyzed polymer nanocomposites was collected by filtration, washed thoroughly with water, and then dried under vacuum (25-50⁰C).

Evaluation of methanol oxidation on Pt loaded (C₆H₄NH)_{0.41} V₂O₅·0.5H₂O nanocomposite

The Pt loaded conducting poly (3, 4-ethylenedioxythiophene) intercalated vanadium pentoxide nanocomposite exhibited excellent activity and stability for methanol oxidation compared to the Pt loaded on the commercial Vulcan XC 72R carbon support. The conducting poly (3, 4-ethylenedioxythiophene) not only acted as an

excellent electronic support for Pt particles but also aided for an increased stability of the layered transition metal oxide, under present electrochemical operating condition

Catalyst	Pt loading $\mu\text{g}/\text{cm}^2$	Methanol oxidation activity mA/cm^2
Pt/(C ₆ H ₄ O ₂ S) _{0.4} V ₂ O ₅ ·0.5H ₂ O	10	28.4
Pt/Vulcan	10	15

CONCLUSIONS

1. The supports for noble metal electro-catalyst have a definite role in the development of electrodes for fuel cells.
2. The functionalization of the support carbon materials is a mean to increase dispersion and also intrinsic activity of the noble metal sites.
3. Oxide supports, though may lead to net loss of energy, can favour the removal of otherwise poisons for the noble metal electro-catalytic sites
4. Conducting polymers and their composites can be conceived as alternate supports for noble metal electrodes for effective dispersion and intrinsic activity.

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PROPOSED CONTENTS OF THE THESIS

CHAPTER 1: Introduction

CHAPTER 2: Experimental

CHAPTER 3: Role of Nitrogen functionality in the carbon nanotube supported electrodes for methanol oxidation

CHAPTER 4: Electro-oxidation of methanol on Pt supported TiO_2 nanotube electrodes

CHAPTER 5: Electrochemical studies on Pt/ WO_3 nanorods electrodes

CHAPTER 6: Template Synthesis and Electro-catalytic activity of Conducting

Nitrogen Functionalized POPD Polymer Nanotube Supports

CHAPTER 7: Synthesis and electrochemical studies on Pt supported PEDOT-V₂O₅ nanocomposite electrodes

CHAPTER 8: Summary and Conclusions

LIST OF PUBLICATIONS BASED ON THE RESEARCH WORK

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1. **T. Maiyalagan and B. Viswanathan** (2005) Template Synthesis and Characterization of Nitrogen Containing Carbon Nanotubes. *Mater. Chem. Phys* (93) 291.
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3. **T. Maiyalagan, B. Viswanathan ,U.V. Varadaraju, B. K. Pradhan, B. Srinivas** (2005) Electro-oxidation of methanol on TiO₂ nanotube electrodes. *Proc. Fuel Cell Seminar*, Palm springs, California, USA 149.
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6. **T. Maiyalagan, B. Viswanathan and U.V. Varadaraju** (2006) Electro-oxidation of Methanol on Pt supported TiO₂ Nanotube *J. Nanosci. Nanotech.* 6, 2067.
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