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TO STUDY ELECTRO CATALYTIC ACTIVITY FOR METHANOL
OXIDATION AND CARBON MONOXIDE TOLERANCE PROPERTY OF
NANOPARTICLES OF BIMETALIC ALLOY CATALYST Pt-Ni, Pt- Pu
AND Pt- Mo

BY

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Work on” TO STUDY ELECTRO CATALYTIC ACTIVITY FOR METHANOL OXIDATION AND CARBON MONOXIDE TOLERANCE PROPERTY OF NANOPARTICLES OF BIMETALIC ALLOY CATALYST Pt-Ni, Pt- Pu AND Pt- Mo” has been supported by UGC. We would like to acknowledge the following for support of this research.

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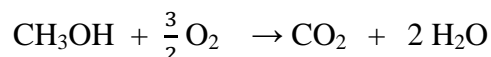
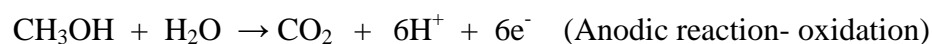
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Introduction: Global warming and greenhouse emissions are two critical issues currently addressed by the scientists all over the world. Some greenhouse gases, such as CO₂, occur naturally and are emitted to the atmosphere through natural processes and human activities. Among the human activities, automobiles, powered by internal combustion engines, are significant producers of harmful greenhouse emissions. For instance, in Canada, about 80% of the anthropogenic emissions of CO₂ during the past 20 years are due to burning fossil fuels and cement production. The amount of greenhouse gas emissions come from the combustion of fossil fuels is about 90%. Recent research also shows that the amount of CO₂ produces from a small car can be reduced by as much as 72% when powered by a fuel cell running on hydrogen reformed from natural gas instead of a gasoline internal combustion engine. In addition, the world's fossil fuel reserve is limited; hence, alternative and green energy sources are required for better future of our next generation. Hydrogen is the most attractive fuel for fuel cells. It has excellent electrochemical reactivity, provides high levels of power density, and has zero emission characteristics. Nevertheless, distribution and storage difficulties currently pose serious disadvantages to the use of pure hydrogen as the feed for fuel cells in automotive-propulsion. Three forms of on-board hydrogen storage are usually considered: compressed gas, liquid hydrogen, and gas dissolved in metal hydrides or carbon nanotubes. Metal hydride systems are the safest of the three, but they have low mass and volumetric energy densities. Liquid hydrogen is complex, expensive, and bulky, and subject to considerable losses during and after refuelling. Storage of practical amounts of H₂ as compressed gas requires very large high-pressure vessels. Distribution of hydrogen also poses difficulties as serious as storage. The infrastructure for its widespread distribution does not yet exist. Nevertheless, eventual cost effective delivery and dispensing of hydrogen can undoubtedly reduce the complexity and cost of fuel cell vehicles, thus enhancing the likelihood for success of the technology. Today, approximately 95% percent of all hydrogen

is produced by steam restructuring of natural gas, the most energy-efficient, large scale method of production. Another choice is to feed liquid fuel directly to the anode. In 1839, William Grove British Physicist first developed the principal of fuel cell. Direct methanol fuel cell is an alternative power source for portable power applications. Direct methanol fuel cell (DMFC) is one such possibility. The advantages of supplying methanol directly to the fuel cell are significant due to consumer acceptance of liquid fuels. Methanol distribution infrastructure exists to some extent already. More importantly, a direct methanol fuel cell system does not require a large and heavy hydrogen loading system. This advantage, in terms of simplicity and cost, means that direct methanol fuel cell presents an attractive alternative to hydrogen, in principle, fed system. The anodic oxidation of methanol is a catalytic reaction in which the CO_2 and six electrons are produces.



Fuel cells are able to produce electricity directly from fuel with a good efficiency. For stationary applications, they would replace the combustion-based electric-generating methods where energy losses occur in the thermal engine as well as in the electric generator. They can be applied to residential, commercial and industrial sectors for electricity as well as for heat production. However, there are some inherent problems with direct methanol fuel cell. The slow anode methanol electro oxidation requires a large overpotential and severely decreases the cell voltage. Furthermore, the perfluorsulfuric-acid based membrane such as Nafion is prone to the problem of methanol crossover, which poisons the cathode O_2 reduction catalyst and reduces the total fuel efficiency as well. Although composite membranes and membranes

different from Nafion are being actively pursued, the achievement so far is limited. The best performance with the most up to date DMFC technology is still too low to be used as a power source. The main factors that limit the practical application of direct methanol fuel cell are the slow kinetics of methanol electrooxidation at anode and the poisoning of electrode surfaces. Therefore, the development of highly effective methanol electrooxidation catalysts seems very attractive. Pt shows a good electrocatalytic activity towards the methanol electrooxidation; however, it is easily poisoned by CO, the intermediates of methanol electrooxidation. Much effort has been made to develop Pt-based catalysts with higher CO poisoning tolerance and electrocatalytic activity. Improved electrocatalytic activity towards the methanol electrooxidation has been reported for Pt-based catalysts with other elements such as Ru, Sn, and Os. Among these Pt-based catalysts, Pt-Ru bimetallic catalyst has shown the best electrocatalytic activity towards the methanol electrooxidation. The improvement of electrocatalytic activity towards the methanol electrooxidation with PtRu catalyst can be ascribed to the bi-functional mechanism. The CO removal process is achieved at Pt-Ru catalyst because of the reaction of Ru-OH groups with neighbouring CO adsorbed on Pt.

Metal nanoparticles possess a high catalytic efficiency and a large surface-to-volume ratio. A large variety of methods including impregnation, colloidal deposition, supercritical fluid, and electrodeposition have been reported for the synthesis of Pt-Ru nanoparticles. The electrochemical route is an effective procedure when compared with others which are intricacy of the fabrication steps and impurity might be involved during the preparation.

The synthesis of Pt-Ru nanoparticles on a suitable catalyst support which provides dispersion and stability is important in the field of direct methanol fuel cell. In recent studies, carbon nanotubes have been considered as a promising material for catalyst support because of their good electrical conductivity, high chemical stability, and large surface-to volume ratio. The applications of transition metal on carbon nano tubes in fuel cells as a catalyst support have

been reported in literature. It is well known that CO binds strongly on Pt at low temperatures, thus, reducing Pt surface sites available for H₂ adsorption and oxidation. Although the electrochemical oxidation of CO with H₂O is thermodynamically favourable, the kinetics are slow, and in practice, a large overpotential is required before electrooxidation occurs. Surface coverage of CO on Pt at even the ppm gas concentrations is very high at typical PEM fuel cell operating temperatures.



Gottesfeld and Pafford have shown that the fuel cell performance is highly dependent on the feed CO concentration. Even 5 ppm CO in hydrogen can cause performance degradation when the current density is over about 400 mA/cm² and the voltage loss is over 300 mV at a current density of 1000 mA/cm². The voltage loss due to CO poisoning is more dramatic initially with an increase in the anode feed CO concentration, at a current density of 700 mA/cm², the voltage loss is over 400 mV for a CO concentration increase from 0 to 20 ppm, while the subsequent voltage loss is only about 100 mV for a further CO concentration increase from 20 to 100 ppm). A more detailed experimental work on the effect of CO concentration on PEM fuel cell performance is reported by Oetjen et al.¹⁴ Both Pt and PtRu catalyst were evaluated using H₂/CO as anode feed with different CO concentration. The results show that with a 100 ppm CO in the anode feed, there is a 60% voltage loss as compared to pure H₂ feed on Pt anode catalyst. On the other hand, at identical experimental conditions, the PtRu (1:1 atomic ratio) anode catalyst provides only about 100 mV voltage loss at a current density of 500 mA/cm². Similar results are given by Acres et al,¹⁵ for a 240 cm² Ballard Mark V cell. They investigated the impact of 10, 40, 100 ppm CO in the hydrogen fuel stream on the performance of a Pt-based anode at a platinum loading of 0.37 mg/cm². Another parameter that determines how CO impacts PEM fuel cell performance is fuel cell temperature. The CO adsorption on Pt surface will become weaker as the

temperature increases. Lee et al¹⁶ showed the effect of temperature on fuel cell performance with a feed of H₂ containing 20 ppm CO. It is shown that the poisoning outcome is much more severe for low temperatures than at higher temperatures. For a cell voltage of 0.4 V, less than 100 mA/cm² could be sustained at 40 ° C. However, a current density of 1500 mA/cm² could be sustained when the cell temperature was increased to 115 ° C. This is an indication that operating PEM fuel cell at higher temperatures can improve the cell performance in the presence of CO. In more recent work, reported the effect of Pt-Ru catalyst loading on the performance of a PEM fuel cell with an anode feed of 10 ppm CO/70% H₂/30 % CO₂. It was found that higher catalyst loading is beneficial to CO tolerance. For example, at a current density of 200 mA/cm², cell voltage is 0.69 V for a loading of 0.19 mg/cm² Pt-Ru. When the catalyst loading is over 0.43 mg/cm², the cell voltage at the same current density can achieve 0.75 V. However, a still higher catalyst loading of 1.06 mg/cm² does not increase the cell voltage. This was ascribed to the higher conducting resistance and mass transport limitations caused by the thicker catalyst layer when the catalyst loading is increased. Since the fuel processing reactor will experience start up, shut down or load change if used in the on-board generation of H₂, there would be concentration changes of CO superimposed on the steady-state CO concentration of 5-50 ppm.¹⁸ Thus, the response of the fuel cell system to the transient change of CO concentration is also of practical interest. Bauman reported the performance decay and recovery in PEM fuel cell in response to step changes in the level of CO in the feed stream. It was found that the transient time is primarily controlled by the CO inlet flux, which depends upon the CO concentration and anode inlet flow rate. Another important observation is that the transient time for a step change from 10 ppm to 200 ppm is much shorter than that for a step change from 0 to 200 ppm. The recovery by hydrogen purge was found to be sluggish and is a function of cell temperature. The rate is thought to be controlled by the rate of the thermal desorption of C. There has been a great

deal of effort invested into overcoming the detrimental effect of CO on the fuel cell performance. The most successful approach to solving anode poisoning problem is the development of CO tolerant electro-catalysts capable of operating in the presence of, e.g., 100 ppm CO. Thus, much effort has been spent in modifying Pt by alloying with other metals to produce catalysts with improved CO tolerance. The most successful alloy thus far is the binary Pt-Ru alloy catalyst. Pt-Ru is also known to be a better catalyst for methanol electrooxidation based on the early work of Watanabe. Later it was shown to have better CO tolerance as well by many other researchers. Further improvement in the preparation and optimization of the Pt-Ru catalyst is still a field of active research. Thus, Schmidt and Paulus tried to simplify the preparation procedure and improve the alloying of Pt with Ru.

An organometallic preparation scheme was employed that can synthesize the colloid Precursors for bimetallic catalyst. However, a recent result reported by Papageorgopoulos seems to challenge the effort in obtaining an alloyed Pt-Ru catalyst. It was found that the non- alloyed PtRu was even better in the electrooxidation of H₂ containing 100 ppm CO. This positive effect was believed to stem from the higher H₂ oxidation activity of non-alloyed Pt compared to that of Pt alloyed with Ru, although Pt and Ru being in close proximity was still necessary for the CO electrooxidation. He introduced a third component such as Os, Au, SnO_x, to the PtRu alloy in an attempt to further improve the H₂ electrooxidation activity in the presence of CO. It was found that the addition of SnO_x resulted in a very poor performance for H₂ oxidation. However, Pt/Ru/WO_x was found to be twice as active as the PtRu catalyst at practical potentials for the electrooxidation of H₂ with 1% CO. Despite the improvements in the CO tolerance of PtRu over Pt, complete tolerance to 100 ppm CO is not yet achievable at low catalyst loadings. Thus, other Pt based alloys have also been investigated as potential CO tolerant anode catalysts for PEM fuel cell. A non Pt-based alloy

is reported by Schmidt Carbon supported PdAu catalyst was prepared via deposition of preformed bimetallic colloidal precursors. It was shown that in the overpotential range relevant to the fuel cell anode (0.1 V- 0.5 V), the performance of PdAu/C catalyst is better than the state-of-the-art PtRu (1:1 atomic ratio) catalyst at 60 ° C in the lower current density range using both 250 ppm and 1000 ppm.

Plenty of research has been done to discover new kind of membrane materials such as, Dow chemical's XVS membrane, 3p energy membrane, organic and inorganic composite membrane etc. The most commonly used membrane is Du Pont's Nafion membrane. Nafion is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer discovered in the late 1960s by Walther Grot of Du Pont's. It is the first of a class of synthetic polymers with ionic properties which are called ionomers. Nafion's unique ionic properties are a result of incorporating perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone. Nafion has received a considerable amount of attention as a proton conductor for proton exchange membrane (PEM) fuel cells because of its exceptional thermal and mechanical stability. The chemical basis of Nafion's superior conductive properties remain a focus of research. Protons on the SO₃H (sulfonic acid) groups leg from one acid site to another. Pores allow movement of cations but the membranes do not conduct anions or electrons. Nafion can be manufactured with various cationic conductivities. Nafion derivatives are first synthesized by the copolymerization of tetrafluoroethylene (TFE) (the monomer in Teflon) and a derivative of a perfluoro (alkyl vinyl ether) with sulfonyl acid fluoride. The latter reagent can be prepared by the pyrolysis of its respective oxide or carboxylic acid to give the olefinated structure.

The resulting product is an -SO₂F-containing thermoplastic that is extruded into films. Hot aqueous NaOH converts these sulfonyl fluoride (-SO₂F) groups into sulfonate groups

($-\text{SO}_3^- \text{Na}^+$). This form of Nafion, referred to as the neutral or salt form, is finally converted to the acid form containing the sulfonic acid ($-\text{SO}_3\text{H}$) groups. Nafion can be cast into thin films by heating in aqueous alcohol at $250\text{ }^\circ\text{C}$ in an autoclave. By this process, Nafion can be used to generate composite films, coat electrodes, or repair damaged membranes. The combination of the stable Teflon backbone with the acidic sulfonic groups gives Nafion its characteristics. It is highly conductive to cations, making it suitable for many membrane applications. It resists chemical attack. According to DuPont, only alkali metals (particularly sodium) can degrade Nafion under normal temperatures and pressures. The Teflon backbone interlaced with the ionic sulfonate groups gives Nafion a high operating temperature, e.g. up to $190\text{ }^\circ\text{C}$, however, in membrane form, this is not possible due to the loss of water and mechanical strength. It is a super acid catalyst. The combination of fluorinated backbone, sulfonic acid groups, and the stabilizing effect of the polymer matrix make Nafion a very strong acid, with $\text{pK}_a \sim -6$. In this respect Nafion resembles the trifluoromethanesulfonic acid, $\text{CF}_3\text{SO}_3\text{H}$, although Nafion is a weaker acid by at least three orders of magnitude.

It is selectively and highly permeable to water. Nafion, a perfluorosulphonic acid, is the commercially available electrolyte membrane, which is widely used in PEMFCs due to its excellent proton conductivity in the order of 10^{-1} S/cm and good mechanical stability.

Though it possesses several advantages, it still has some disadvantages such as high cost, permeability of methanol through membrane in DMFCs and fluorine content which is not eco-friendly. In order to overcome these disadvantages many research works are being carried out on hydrocarbon membranes like polysulphone, polystyrene, poly ether ether ketones, polyvinylidene fluoride (PVDF), poly ethylene oxide and poly propylene oxide.

Problems in Direct methanol fuel cell:

Various seeming intermediates are formed during methanol electro-oxidation.

Methanol is mainly decomposed to CO which is then further oxidized to CO₂. Other CO like species are also formed: COHads, HCOads, HCOOads]. Principle by-products are formaldehyde and formic acid. Some of these intermediates are not readily oxidizable and remain strongly adsorbed to the catalyst surface. Consequently, they avert fresh methanol molecules from adsorbing and undergoing further reaction. Thus electrooxidation of intermediates is the rate limiting step. This poisoning of the catalyst surface seriously slows down the oxidation reaction. Besides, a small percentage of the intermediates desorbs before being oxidized to CO₂ and hence reduce fuel efficiency but undergoing in complete oxidation. Thus, a very important challenge is to develop new electro-catalysts that inhibit the poisoning and increase the rate of the reaction. At the same time, they should have a better activity toward carbon dioxide formation.

Methanol Crossover is another problem in direct methanol fuel cell. In PEM fuel cells, one of the objectives of the membrane is to stop fuel and oxygen to reach the electrode on the other side and undergo non-electrochemical oxidation. However, in DMFC, the fuel diffuses through Nafion membrane. Due to the hydroxyl group and its hydrophilic properties, methanol interacts with the ion exchange sites and is pulled by hydronium ions in addition to diffusion as a result of concentration gradient between anode and cathode. Methanol that crosses over reacts directly with oxygen at the cathode. Electrons are brought directly from the anode to the cathode along with methanol resulting in an internal short circuiting and consequently a loss of current. Besides, the cathode catalyst, which is pure platinum, is fouled by methanol oxidations intermediates similar to anode.

Methodology:

The most significant part of a direct methanol fuel cell is the membrane electrode assembly (MEA). Its basic structure consists of the polymer electrolyte membrane (PEM), two catalyst layers and two diffusion layers. The polymer electrolyte membrane, which separates the anode and the cathode compartment, preferably allows for proton transport. The anodic and cathodic electrochemical reactions take place within the connected catalyst layers directly attached to the surface of the polymer electrolyte membrane (PEM). The diffusion layers on either side of the membrane electrode assembly MEA provide for good electrical contact of the catalyst layers across the whole surface. All experiments were carried out using,

- i) Nafion 117 resin, a per fluorinated ion exchange polymer membrane.
- ii) Carbon-supported platinum molybdenum bi metallic anode catalyst.
- iii) Carbon- supported platinum Nickel bi metallic anode catalyst.
- iv) Carbon- supported platinum molybdenum bi metallic anode catalyst.

Nafion 117 resin, a per fluorinated ion exchange polymer membrane were treated with $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ -Tetra ethoxy silane (TEOS) and Titanium isopropoxide ($\text{Ti}(\text{O}-i\text{-Pr})_4$) mixture solution in methanol in variable % composition. This was developed using a situ-sol-gel technique. Methanol permeability of the composite membrane was evaluated. The solid proton exchange membrane was then assimilated with bimetallic alloy catalyst of Pt-Ni, and, Pt-Mo. Various % composition of catalysts composed of about platinum – molybdenum and platinum - nickel were prepared on a graphitized carbon black paper. Solution of ammonium Molybdenum sulphate in methanol for Mo, solution of $[\text{Pt}-(4(2\text{-methoxybenzylidene amino})-1,5\text{ dimethyl-2 phenyl-1 H pyrazol- 3(H)phenyl-hydrazin})_2]\text{Cl}_4$ for Pt were used to load catalyst on carbon support NCK-77 (thickness= 210 μm). After deposition of the active components, the substrate was subjected to reduction and neutralization. All samples

were subjected to thermal treatment for 1 h at 1173K. Structural information about the catalysts was received from X-ray diffraction (XRD) analysis. Varying percentage of bimetallic/C catalyst on carbon paper was used to prepare the anode. Nafion 117 proton-exchange membranes (Du Pont) was used after sequential treatment with 2% H₂O₂, deionized water, 0.5 M H₂SO₄ and again with deionized water in order to remove any inorganic and organic impurities. The membrane electrode assembly (MEA) was prepared by hot pressing in a Model C Carver hot press at 130 °C and under a pressure for about 2 minutes. The fuel cell performance were studied at different concentration of CO by varying anode flow rate. The methanol solution of various concentrations (0.5 - 3 mol/L) was served into the anode at a flow rate of 0.5- 10 mL/min. Oxygen was served to the cathode at 150 mL/min. The measurement is generally conducted using a three-electrode setup, working electrode, counter electrode and reference electrode. In case of non-zero net current on the electrode, it is essential to minimize the I R drop in the electrolyte, e.g., by positioning the reference electrode near the surface of the working electrode , or by using a supporting electrolyte of sufficiently high conductivity.. The potential measurements are performed with the positive terminal of the electrometer connected to working electrode and the negative terminal to the reference electrode.

Experimental:

Preparation of Nafion/SiO₂/ TiO₂ composite membranes:

Nafion/SiO₂/ TiO₂ composite membranes were prepared via in situ sol gel reaction. Firstly, the Nafion 117 membrane was dried at 80°C for five hrs. Then the membrane was dipped into the methanol/water solution and kept for 1 hr. Afterwards, the sample was rubbed out with filter paper. The membrane was then immersed into various proportion of CH₃OH-H₂O/C₂H₅OH-Tetra ethoxy silane(TEOS)/Titanium isopropoxide(Ti(O-i-Pr)₄) mixture solution for five minutes and then membranes were soaked in 0.5 M H₂SO₄ for one hour. Finally membranes were rinsed with deionised water. Different reaction concentrations adopted are as shown as in table no. 01.

Table No.01

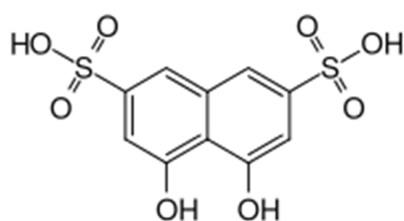
	CH ₃ OH	H ₂ O	TEOS	Ti(O-i-Pr) ₄
1	40 cm ³	05 cm ³	05 cm ³	00 cm ³
2	30 cm ³	10 cm ³	10 cm ³	00 cm ³
3	40 cm ³	05 cm ³	00 cm ³	05 cm ³
4	30 cm ³	10 cm ³	00 cm ³	10 cm ³
5	30 cm ³	10 cm ³	05 cm ³	05 cm ³
6	25 cm ³	10 cm ³	10 cm ³	05 cm ³
7	25 cm ³	10 cm ³	05 cm ³	10 cm ³

Methanol, oxygen permeability:

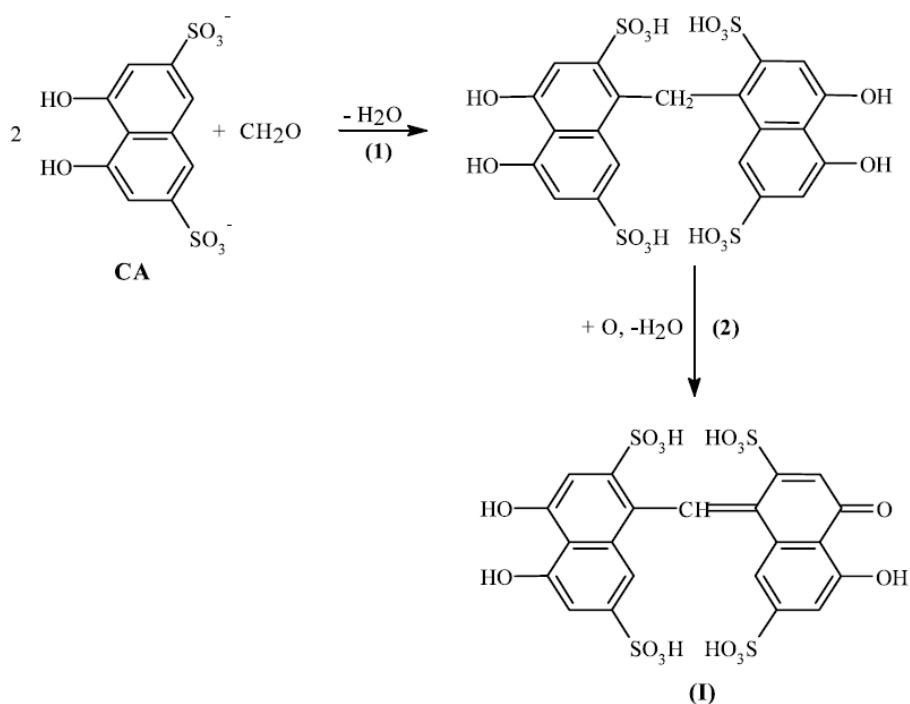
The crossover of methanol is subjective to membrane characteristics, temperature, the operating current density. In general, an increase in temperature causes an increase in the diffusion coefficient of methanol. These effects contribute to an increase in the methanol crossover rate. The crossover includes both methanol permeability due to a concentration gradient and molecular transport caused by electro-osmotic drag in the presence of a proton conducting electrolyte. The latter is directly related to the proton migration through the membrane and it increases with the current density. In a polarization curve, the commencement of diffusional limitations occurs when the rate of reactant supply is lower than the rate of its electrochemical consumption. Thus, if the anode is sufficiently active to oxidize methanol electrochemically to CO₂ at a rate comparable to or higher than the rate of the methanol supply, the methanol concentration gradient between anode - electrolyte and cathode-electrolyte interfaces could be reduced significantly. Membranes that are very thick are effective barriers for reducing methanol crossover; in opposition, an increase in thickness causes an increase of ohmic over potentials. In some cases, it may be more dynamic to use a thinner membrane with reduced ohmic limitations and select appropriate operating circumstances which limit the methanol crossover.

Experiment to evaluate methanol permeability was carried out using a diaphragm diffusion cell, consisting of two reservoirs separated by an electrolyte membrane with a dense layer of composite membranes to reproduce a phenomenon of methanol crossover in DMFC system. The PEM is sandwiched between compartments. Initially the one compartment was filled with 50 ml of aqueous methanol solution and other compartment with 50 ml of deionized water. The solution in each bath was stirred using magnetic stirrer during measurement to

keep uniform concentration. Due to the presence of liquid water on either side of the cell, the membrane remains hydrated. Equal amount of solution in both the compartments ensures that equal hydrostatic pressure is maintained. The change in concentration of methanol in receptor compartment was measured for various composite membranes. The methanol permeability across the Nafion 117/ SiO₂/ TiO₂ composite membrane was measured by taking 50 ml of 5% ,10%and 30% methanolic solution on one side of the membrane and 50 ml of water on other side the membrane was equilibrated. In this condition liquid sample of 50 μL were taken every 30 min. from the permeate compartment and analysis was carried out by colorimetric micro-determination method using chromotropic acid as reagent as given below



chromotropic acid reagent.



Colorimetric micro-determination of methanol:

10 cc of sample solution in 50 cc standard measuring flask was treated with H_3PO_4 and KMnO_4 solution. The solution was kept for 10 min at room temperature with occasional swirling to ensure oxidation of methanol to formaldehyde. Sodium bisulphite is then added dropwise to reduce excess of KMnO_4 . Solution was cooled and kept in ice bath and 4 ml of cold conc. H_2SO_4 and four drops of chromotropic acid reagent were added. Flask was kept in water bath at 60°C for 15 min. The solution was diluted up to the mark with distilled water. Using distilled water as a blank, absorbance of the solution and standard were measured at 580nm.

The methanol molecule diffuses along the concentration gradient through membrane into the opposite compartment of the diffusion cell. This induces concentration gradient hence, diffusion coefficient is obtained by equation,

$$C_B = \frac{A}{V_B} \times \frac{DK}{L} \times C_A (t - t_0) \quad \text{where,}$$

A = effective area of membrane.

L = thickness of membrane.

C_A = methanol concentration in feed compartment in mol / dm^3 .

C_B = methanol concentration in permeate compartment mol / dm^3

D = Methanol diffusivity (m^2 / sec)

t_0 = is time lag (sec).

$$t_0 = L^2 / \sigma D$$

Methanolic permeability Γ is defined as product of the diffusivity of methanol D and partition coefficient K .

$$\Gamma = D \times K$$

The methanol concentration in diffusion reservoir C_B at t was calculated from the linear interpolation C_B at t was calculated from the linear interpolation of C_B v/s t and the slope of the graph can be written as follow,

$$M = \frac{C_B(t)}{t - t_0}$$

Therefore, the above equation can be rearranged to calculate the methanol permeability as expressed below,

$$\Gamma = m \frac{V_B L}{A C_A}$$

From the slope of the plot, the membrane methanol permeability was found to be $DK = 1.27 \times 10^{-6} \text{cm}^2$. The partition coefficient between the membrane and the adjacent solution (K) is dimensionless. Methanol cross over using Nafion 117 with 1:1 TEOS and $\text{Ti}(\text{O-i-Pr})_4$ was found to be minimum. By using appropriate cell design, treating Nafion 117 with 1:1 TEOS and $\text{Ti}(\text{O-i-Pr})_4$ significant drop in methanol crossover was achieved.

Preparation of precursor complexes:

For DMFC anode catalyst, Pt-Ni/C and Pt-Mo/C metal alloy on carbon NCK-77 were prepared using molecular precursors as a source of metal.

The synthesis strategy employed involves ,

- i) Preparation of molecular precursor molecule/complex.
- ii) Absorption of precursor molecule from solution onto carbon support giving a precursor/carbon composite material.
- iii) Reactive thermal degradation of the surface support precursor molecules depositing the core metal atoms on the surface of the carbon support.
- iv) Thermal annealing to initiate metal migration on the surface of the support leading to formation of Pt-Ni, Pt-Mo alloy nano-crystals.

Metal alloy loading is controlled by adjusting the relative masses of precursor compound and carbon support used as reagent.

For experimental convenience of application, the following research criteria was adopted.

- i) Precursor complex should be comparatively easily prepared and should possess relatively moderate stability to permit easy installation of metal onto carbon support.
- ii) Ligand molecule should have relatively higher molecular weight to deposit nano metal crystal on the carbon support.
- iii) Precursor complex should have sufficient solubility in common organic solvent like methanol, ethanol etc, for effective solution phase absorption or deposition onto a carbon support.

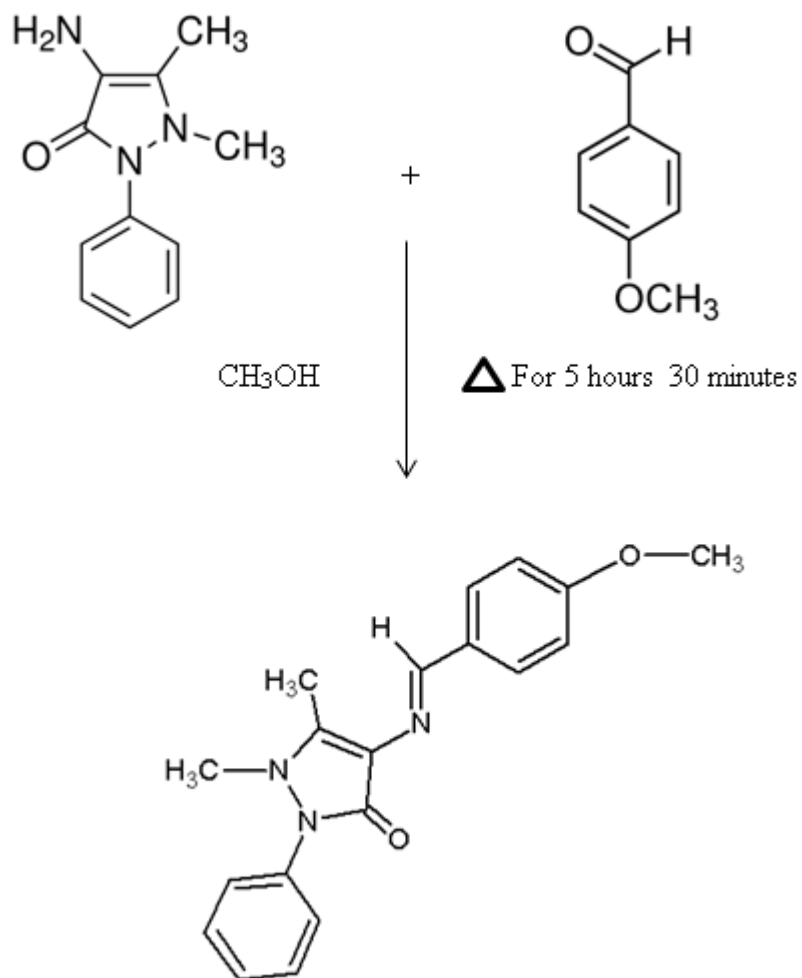
- iv) Condition of reactive degradation of precursor complex should produce Pt-Ni, Pt-Mo nano crystals.
- v) Pt-Ni, Pt-Mo nano composite synthesis should produce gram-scale quantities of a desired nano composite by reproducible synthesis procedure.

Molybdenum ammonium sulphate, [Pt-(4(2-methoxybenzylidene amino)-1,5 dimethyl-2 phenyl-1 H pyrazol-3(H)phenyl-hydrazin)₂] complex and, [Ni-(4(2-methoxybenzylidene amino)-1,5 dimethyl-2 phenyl-1 H pyrazol-3(H)phenyl-hydrazin)₂] complex reagents have been used as precursors.

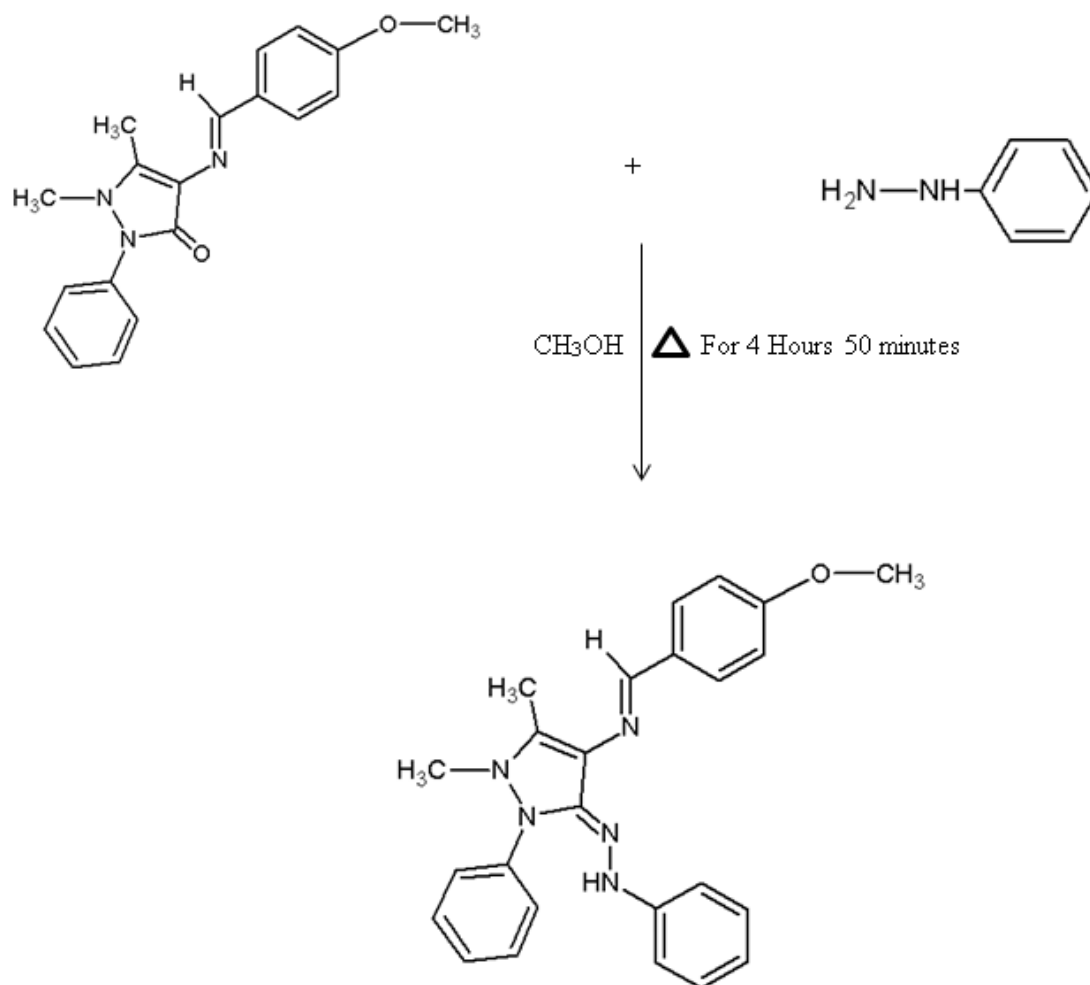
Synthesis of new compound, 4[2-methoxybenzylidene amino]-1,5 dimethyl-2 phenyl-1 H pyrazol-3(H)phenyl-hydrazin has been obtained through the reaction of 4-amino antipyrine with anisaldehyde and phenylhydrazine.

A mixture of 1.78g of 4-amino antipyrine, 1.83g of anisaldehyde in 50cc of ether and 30 cc of methanol was refluxed for 5.30hrs. After that derivative was filtered and purified by recrystallisation.

The intermediate product was further treated with phenylhydrazine. 3.4g of product was refluxed with 2.0g of phenylhydrazine in 40cc of methanol for 4.5 hrs. White coloured moderately stable reagent was synthesised.

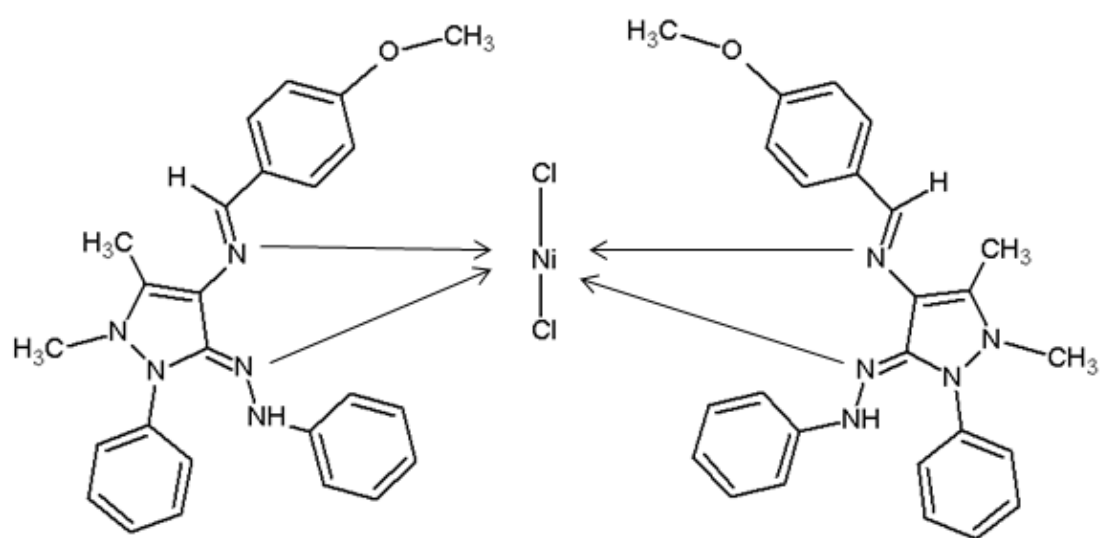
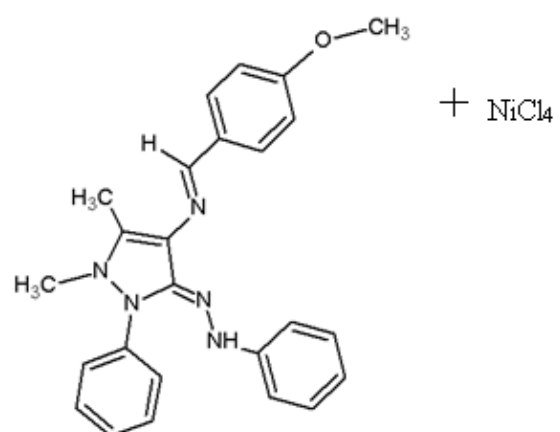


4-[[*E*)-(4-methoxyphenyl)methylidene]amino}-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one

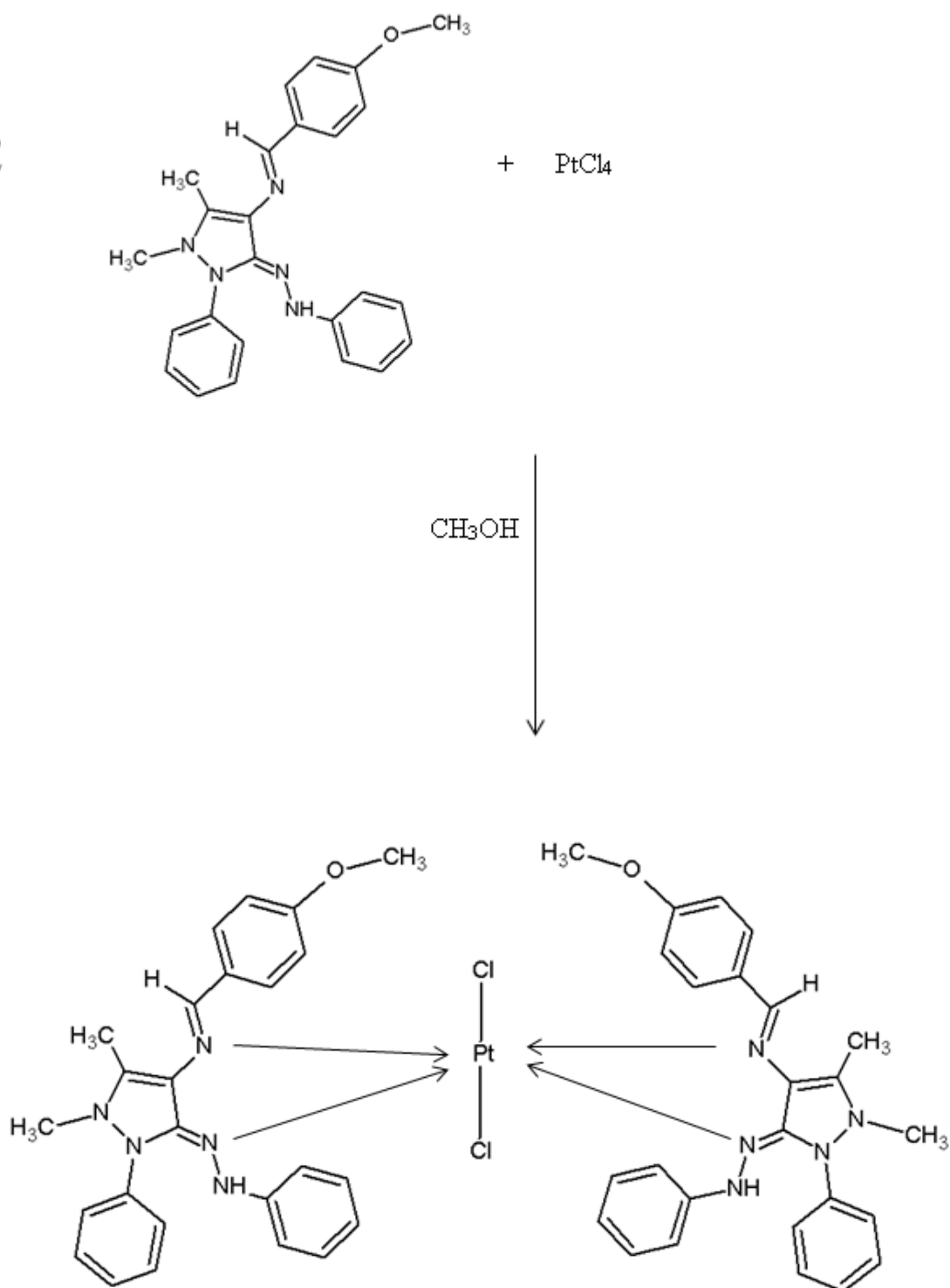


Using the above newly prepared reagent Ni and Pt complexes were prepared. A solution of $\text{NiCl}_4 \cdot 6\text{H}_2\text{O}$ in methanol was added drop wise to the solution of reagent in methanol. The mixture was stirred at room temperature for four hrs. and then evaporated to 90°C until the solution darken. Light pink colour complex was obtained which were filtered and washed with ethanol water mixture and then ethyl ether. Similarly, a solution of PtCl_4 was treated with reagent to obtain purpul coloured Pt complex.

2



2



Pt-Ni/C and Pt-Mo nano composites were prepared using repetitive deposition to ensure both high total metal loading and formation of well dispersed Pt-Ni and Pt-Mo alloy nano crystals. Following each cycle of precursor deposition , the precursor/C composite is heated up to 280°C . Pt/C, Ni/C

And Mo/C have been characterised by XRD.

XRD is powerful method to characterize bulk composition and crystallite size of metal on C support.

The diffraction peak suggest that the prepared Pt/C, Ni/C and Mo/C exist in small partical size.

The average size of metal was estimated by using Scherre's equation,

$$D = 0.94 \lambda_{K\alpha 1} / B_{2\theta} \cos\theta_B$$

Where,

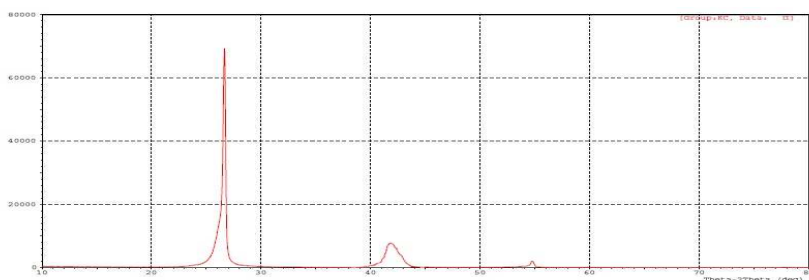
d is the average crystallite diameter,

$\lambda_{K\alpha 1}$ wave length of X ray radiation,

θ_B is the angle of (220) crystallographic plane,

$B_{2\theta}$ is the width in radians of the diffraction peak at half height.

i) Pt/c

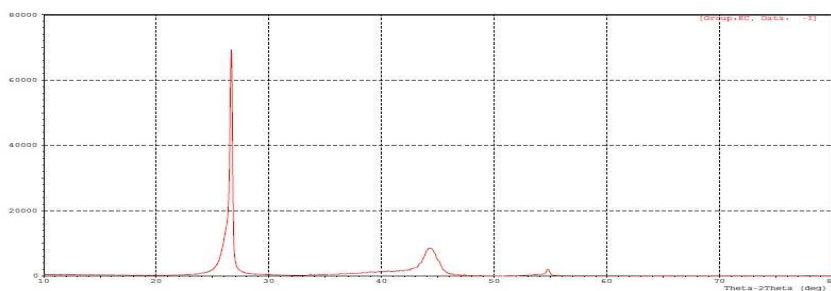


$$D = 0.94 \lambda_{K\alpha 1} / B_{2\theta} \cos\theta_B$$

$$= 0.9 \times 11 \times 10^{-9} / 2 \times \cos 42$$

$$= 6.6 \text{ nm}$$

ii) Ni/C

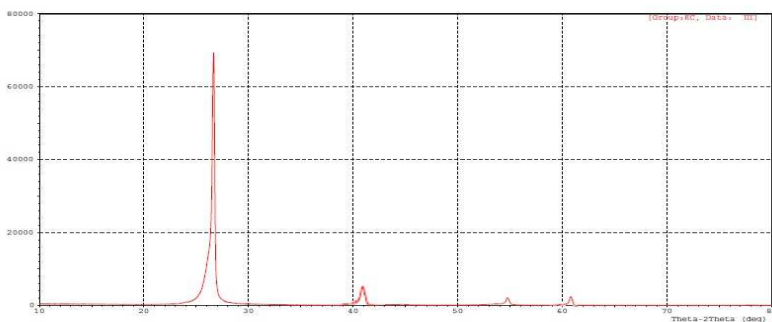


$$D = 0.94 \lambda_{K\alpha 1} / B_{2\theta} \cos\theta_B$$

$$= 0.9 \times 11 \times 10^{-9} / 3.5 \times \cos 45$$

$$= 4.000 \text{ nm}$$

iii) Mo/c



$$\begin{aligned}
 D &= 0.94 \lambda_{\text{Kd}1} / B_{2\theta} \cos\theta_B \\
 &= 0.9 \times 11 \times 10^{-9} / 2 \times \cos 41 \\
 &= 6.5 \text{ nm}
 \end{aligned}$$

The membrane-electrode assembly set up :

The cell typically consists of graphite bipolar plates, gaskets, two electrodes and an ion conducting membrane. The bipolar plates are pressed against the electrode with gaskets for sealing and collecting current. The membrane-electrode assembly (MEA), which consists of the proton

conducting membrane sandwiched between two electrodes (anode and cathode), is the

heart of a PEM fuel cell. In each electrode, there is a catalyst layer and a gas-diffusion

backing layer. The membrane-electrode assembly (MEA), which consists of the proton

conducting membrane sandwiched between two electrodes anode and cathode. In each

electrode, there is a catalyst layer and a gas-diffusion backing layer. The membrane electrode

assembly having an active area of 9.0 cm · 9.0 cm was fabricated employing a Nafion 117

membrane and two electrodes. The employed Nafion 117 membrane with a thickness of 125

µm was pre-treated in this work. The pre-treatment procedures included boiling the membrane

in 5 vol.% H₂O₂, washing in DI water, boiling in 0.5 M H₂SO₄ and washing in DI water for 1

h in turn. Nafion/SiO₂/ TiO₂ composite membranes were prepared via in situ sol gel reaction.

Firstly, the Nafion 117 membrane was dried at 80°C for five hrs. Then the membrane was

dipped into the methanol/water solution and kept for 1 hr. Afterwards, the sample was

rubbed out with filter paper. The membrane was then immersed into various proportion of

$\text{CH}_3\text{OH-H}_2\text{O/C}_2\text{H}_5\text{OH-Tetra ethoxy silane(TEOS)/Titanium isopropoxide(Ti(O-i-Pr)}_4$)mixture solution for five minutes and then membranes were soaked in 0.5 M H_2SO_4 for one hour. Finally membranes were rinsed with deionised water. Composite membrane was placed between the two catalytic electrodes which were supported by graphite gas diffusion layers. This catalyst layer is in good contact with the membrane, which serves as the electrolyte and the gas separator in the cell. The membrane electrode assembly was fixed between two bipolar grooved graphite plate which were designed to serve methanol and oxygen. The catalysts for the anode were loaded with Pt-Ni/C and Pt-Mo/C each metal were loaded 1g/cm^2 . the catalyst for cathode was loaded Pt/C. cathode Pt loading were 2.0 mg/cm^2 .

The methanol solution containing 50 ppm CO of several concentrations of methanol (0.5 - 3 mol/L) was served into the anode at a flow rate of 0.5 - 5 mL/min. Oxygen was served to the cathode at 150 mL/min with humidification. Figure 1 shows the cell performance at 300 K and that at 353 K for comparison. The methanol flow rate was varied from 0.5 to 05 mL/min. The performance of the DMFC system dropped at 318 K for all flow rates in comparison with 353K. The lower flow rate showed a slightly better performance. At 333 K, both the open circuit voltage and the current density at 0.4V decreased with increasing flow rate. Although a similar tendency was observed at 318 K, the dependence of the methanol flow rate on the DMFC performance was small because of the low temperature. Figure 1 shows the cell performance at 318 K at different methanol concentrations with the flow rate of 0.5 mL/min. The open circuit voltage decreased with increasing the methanol concentration to 3 mol/L, because the crossover of methanol formed a mixed potential. In case of the methanol concentration of 1.5 mol/L, The current density seemed to approach a limiting value. The study shows that in the overpotential range relevant to the fuel cell anode 0.1 V- 0.5 V, the performance of Pt-Mo/C catalyst is better than the Pt-Ni/C catalyst at 60 °C in the lower current density range using 50 ppm CO.

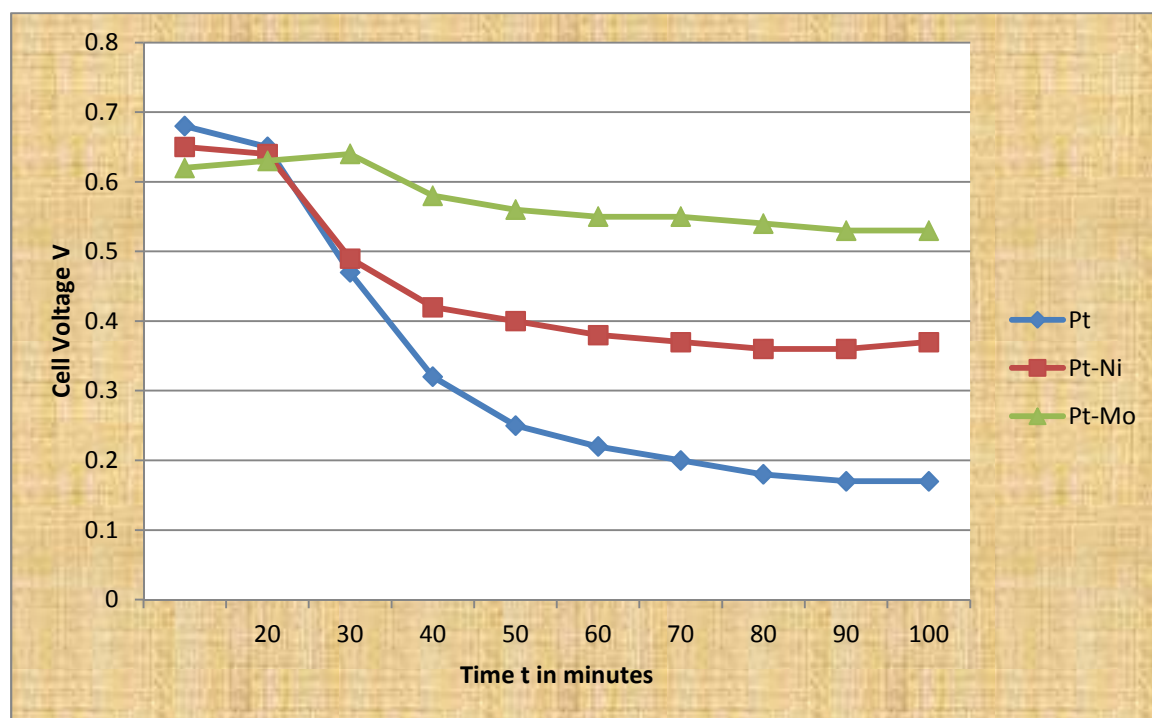


Fig.1 anode feed 2M methanol 0.5 ml/min, cathode feed O₂ 150ml/min at 318K

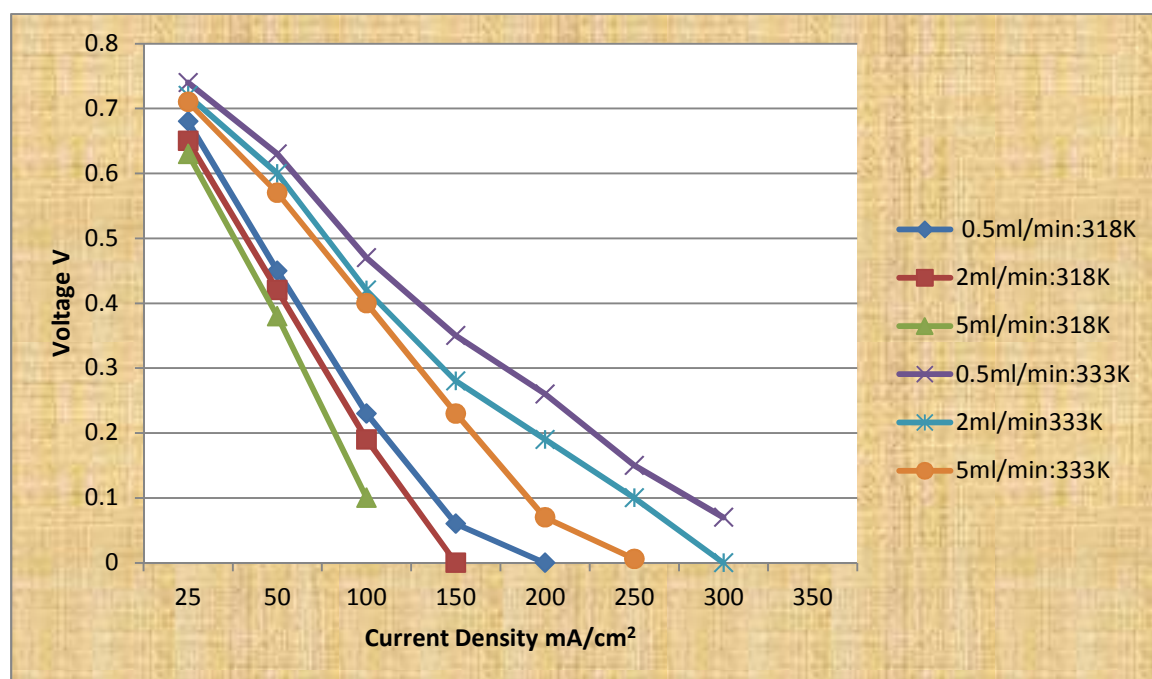


fig.2 Anode catalyst- pt-/C anode feed 2M methanol.

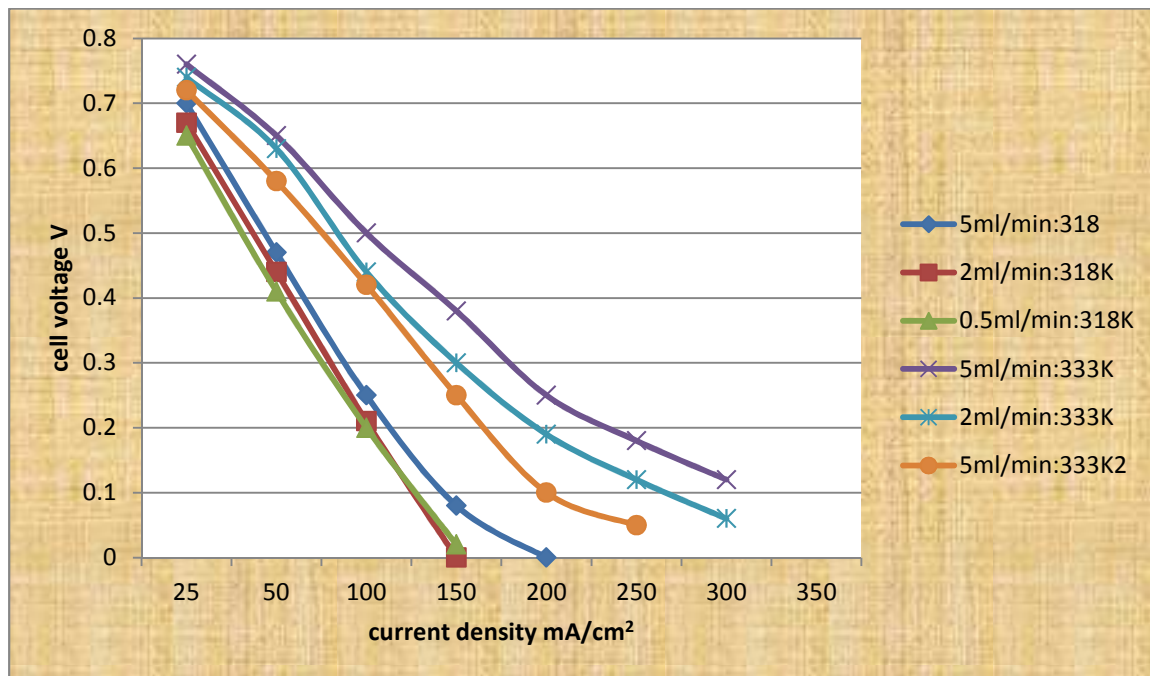


fig.3 Anode catalyst- pt-Ni/C anode feed 2M methanol.

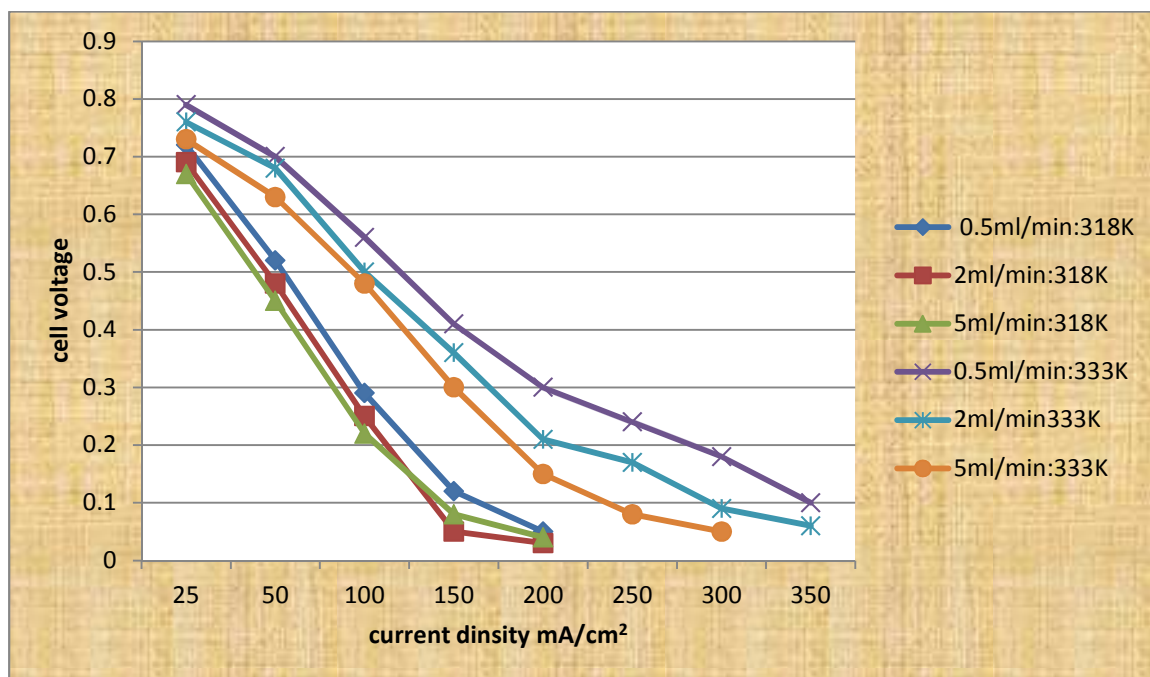


fig.4 Anode catalyst- pt-Mo/C anode feed 2M methanol.

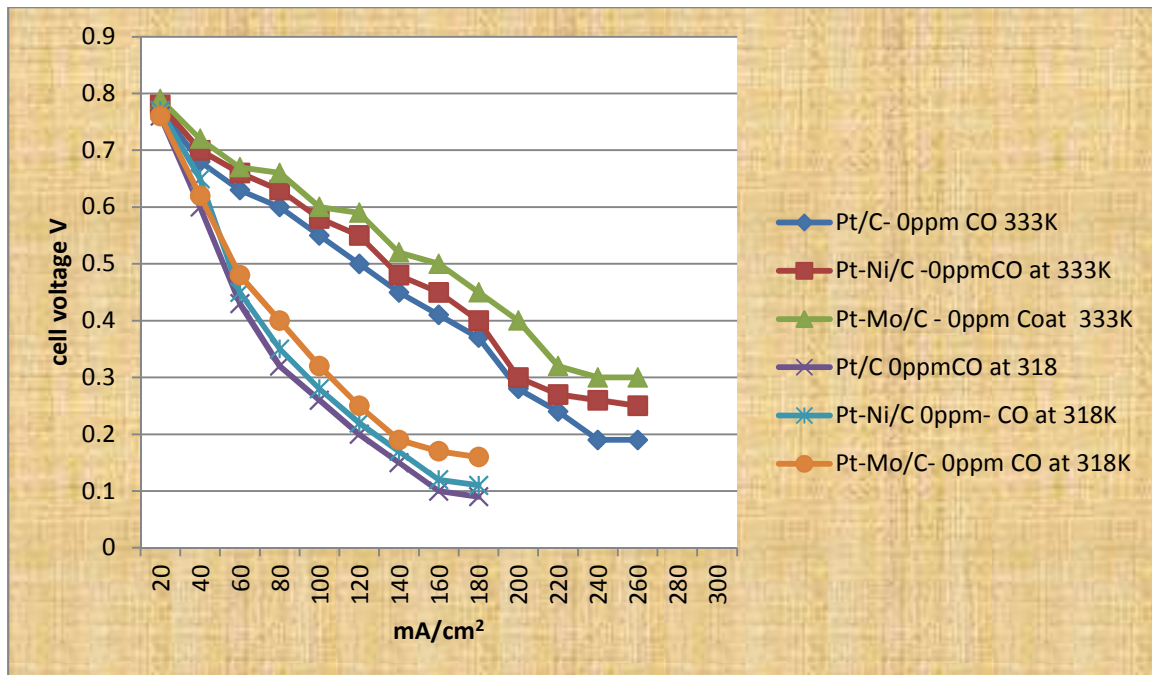


Fig 5 anode flow rate 0.5 ml 1M methanol /min

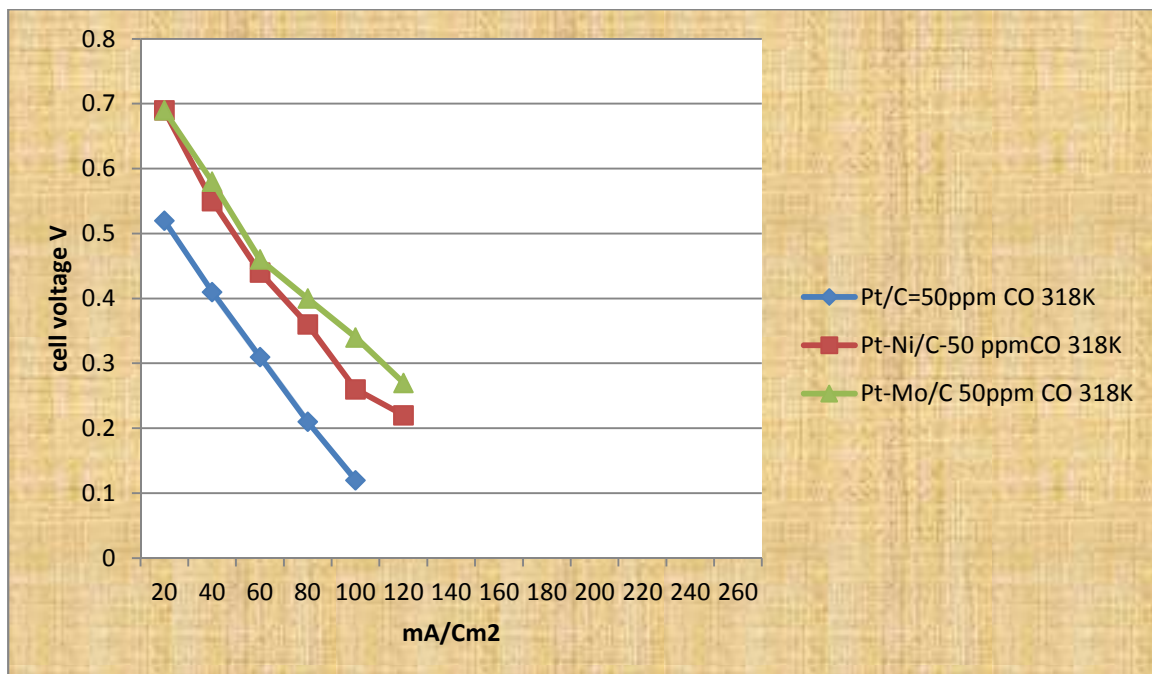


Fig 6 anode flow rate 0.5 ml 1M methano with 150 ppm dissolved CO /min

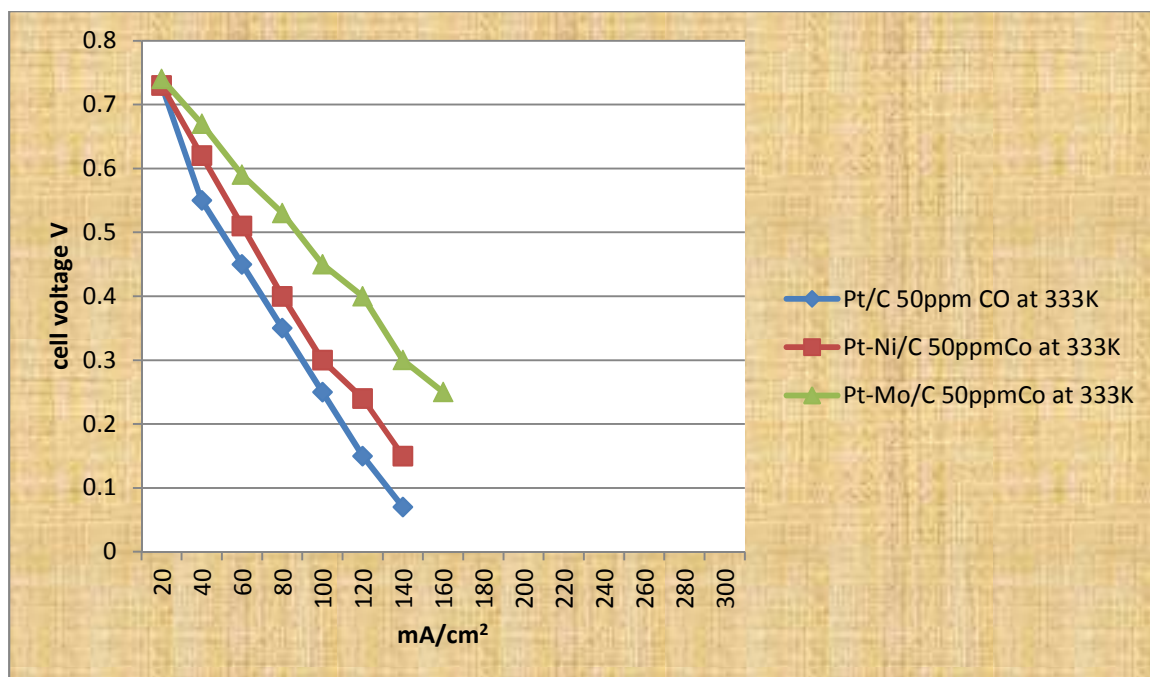


Fig 7 anode flow rate 0.5 ml 1M methanol 50 ppm dissolved CO /min at 333

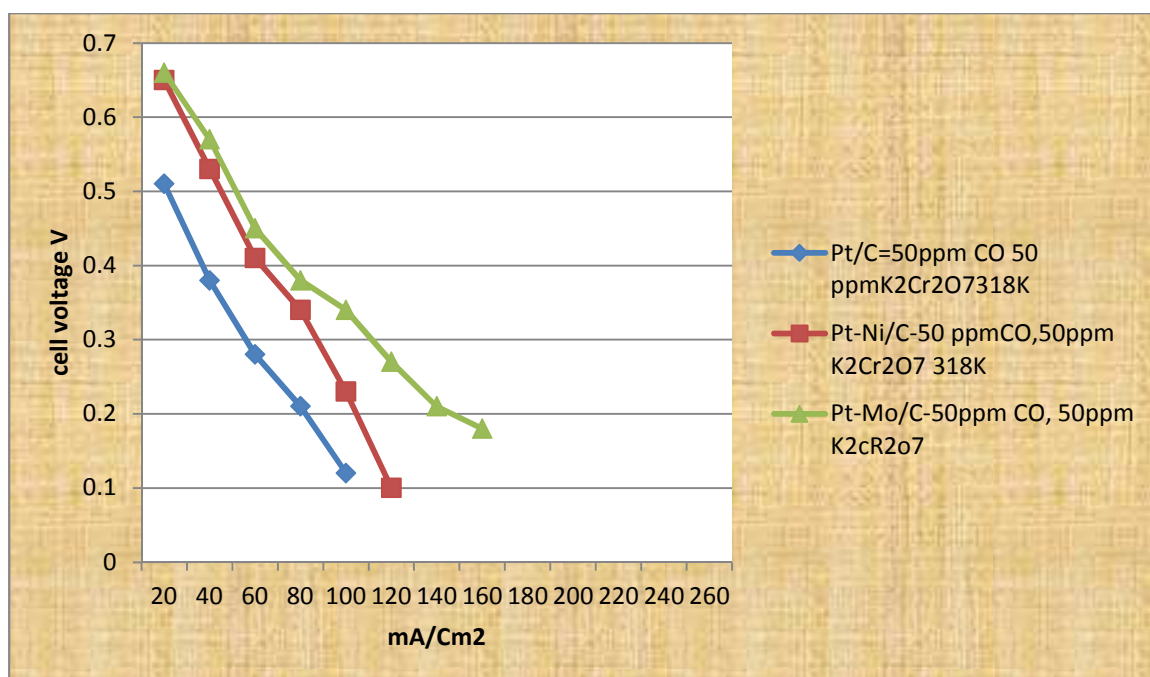


Fig 8 anode flow rate 0.5 ml 1M methanol with 50 ppm dissolved CO and 50 ppm K₂Cr₂O₇ /min

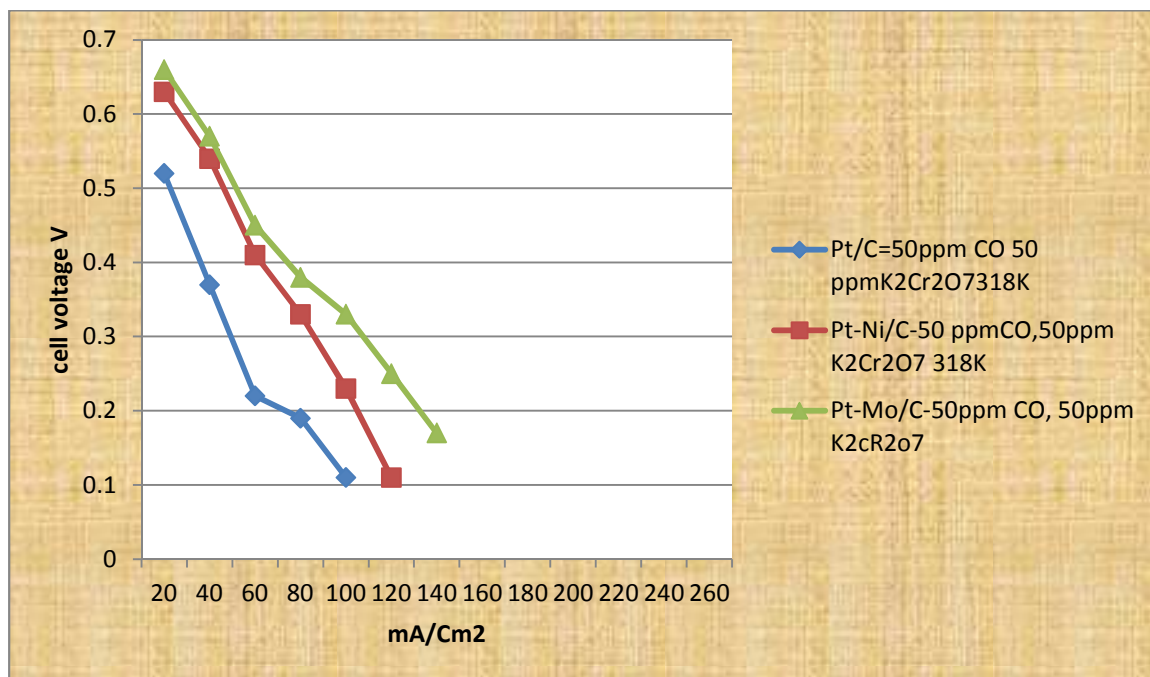


Fig 9. anode flow rate 0.5 ml /min 1M methanol with 50 ppm dissolved CO and 50 ppm K_2CrO_4

Result and discussion: Experiment to evaluate methanol permeability was carried out using a diaphragm diffusion cell, consisting of two reservoirs separated by an electrolyte membrane with a dense layer of composite membranes to reproduce a phenomenon of methanol crossover in DMFC system. using appropriate cell design, treating Nafion 117 with 1:1TEOS and $Ti(O-i-Pr)_4$ significant drop in methanol crossover was achieved.

XRD image 1 for Pt/C shows the partial size of 6.6nm of Pt on carbon support NCK-77.

XRD. image 2

forNi/C shows partial size of 4nm on carbon support NCK-77 . XRD image 3 for Mo/C show the partial size of 6.5 nm on the C carbon support NCK-77.

Variation of cell voltage with respect to time at constant current density shows the better performance of Pt-Mo catalyst . Fig 1 shows the maximum drop of 500mV in cell voltage when Pt/C was used as catalyst. The performance of Pt-Ni is comparatively better than Pt/c as vottage drop was 280mV .the minimum voltage drop of 80 mV was observed for Pt-Mo /C catalyst. This shows that catalytic activity of Pt/C <Pt-Ni/C<Pt-Mo/C.

Figure 2,3 and 4 shows the cell performance at 318 K and that at 333 K for c. The methanol flow rate was varied from 0.5 to 5 mL/min. The performance of the DMFC system dropped at 318 K for all flow rates in comparison with 333K. The lower flow rate showed a slightly better performance. At 333. Both the open circuit voltage and the current density decreased with increasing flow rate. Although a similar tendency was observed at 318 K, the dependence of the methanol

flow rate on the DMFC performance was small because of the low temperature.

Figure 2 ,3 and 4 shows the cell performance at 318 K/333K at different methanol concentrations with the flow rate of 0.5 mL to 5 mi/min. The open circuit voltage decreased

with increasing the methanol concentration to 3 mol/L, because the crossover of methanol formed a mixed potential.

It is observed from the graph that cell performance is better at higher temperature and lower rate of anode feed.

Variation of Cell voltage with respect to current density Fig. 5 shows the better catalytic activity of Pt-Mo/C over Pt-Ni/C and Pt/C. Performance of Pt-Ni/C is found to be better than Pt/C.

Addition of 50 ppm CO in the anode flow degrades catalyst this can be shown by potential drop (Fig. 5, 6, 7). In presence of CO Pt-Mo/C was found to be showing more tolerance towards CO compared to Pt/C and Pt/C. The effect of addition of 50 ppm K₂Cr₂O₇ and K₂CrO₄ in the stream of methanol and CO was not found to have positive effect on the system. It is observed that cell voltage further decreases on addition of K₂Cr₂O₇ and K₂CrO₄.

Effect of temperature on surface process at Pt(III) - H, oxide formation and CO oxidation are well studied; J. Phys. Chem. B 1999, 103, 8568-8577, N.M. Markovic, T.J. Schmidt & others. The chemisorption bond energy of the OH ad state is reported to be temperature dependent. Pt-OH bond energy is reported as -136 kJ/mol. Gibbs energy of adsorption $\Delta G_{H_{2}O}$ is a function of coverage at varying temperature is given by Langmuir equation assuming 1st order kinetics as,

$$\frac{\theta}{1-\theta} = \exp\left(-\frac{E_{rhe}F}{RT}\right) \exp\left(-\Delta G_{H_{2}O} \frac{\theta}{RT}\right) \quad \text{--- -- -- -- -- 1}$$

The Gibbs energy of adsorption is assumed to vary linearly with coverage,

$$\Delta G_{Hupd} = \Delta G_{Hupd} \theta = 0 + \gamma\theta \text{-----} -2$$

Eqn 1 & 2 produces ,

$$\frac{\theta}{1-\theta} \exp\left(\gamma \frac{\theta}{RT}\right) = \exp\left(-\frac{E_{rheF}}{RT}\right) * \exp\left(-\Delta G_{upd} \theta = \frac{0}{RT}\right) \text{-----} -3$$

$\Delta G_{Hupd} \theta = 0$ is initial zero coverage energy of adsorption . equation 3 produces a linear θ v/s E relation for intermediate value of θ , since the term $\theta/(1-\theta) = 1$ and very much more slowly with E than the exponential terms.

The apparent free energy of adsorption at any given temperature is characterised by two parameters $\Delta G_{upd} \theta=0$ and interaction parameter f ; $f = \gamma/RT$.

The isosteric heat of adsorption can be obtained from temperature dependence of gibbs free energy of adsorption q_{Hst} from the relation

$$q_{Hst} = \partial \left(\frac{\Delta G_{upd}}{T} \right) \frac{\theta}{\partial T^{-1}}$$

and the entropy of adsorption from the relation

$$\Delta S_{upd} = \partial \partial (\Delta G_{upd}) \frac{\theta}{\partial T^{-1}}$$

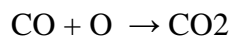
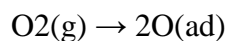
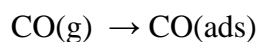
has been reported that heat of adsorption show linear variation with θ up from 42kj/mol to 24kj/mol.

The $pt - OH$ bond energy was estimated as 350kj/mol.

The heat of adsorption of co on the surface of pt - varies from 140kj/mol to 45 kj/mol.

Journal of physical chemistry vo.92.

The langmuir – Hinshelwood reaction between adsorbed CO and O atom is well studied and given as ,



From the above rate expression can be formulated as ,

$$\Delta d \frac{\{CO_2\}}{dt} \rightarrow K_{exp} \left(- \frac{E_{desCO}}{RT} \right) \frac{P_{O_2}}{P_{CO}}$$

The activation energy varies from 33 to 13 k cal/mol.

Pu 238 is a radio active isotop and very powerful α emmitter. Plutonium-238 is a special material that emits steady heat due to its natural radioactive decay. Several unique features of plutonium-238 have made it the material of choice to help produce electrical powe

Plutonium-238 has a specific power of 0.56 watts/gm. Pu in form of Plutonium oxide dopted pt-Pu/C catalystr is assumed to have maximum tolerance towards CO as Pu acts as a continuas source of thermal energy for longer period .

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