

# Electro-Catalytic Activity of Nano-Sized Pt-Ni Bimetallic Alloy Particles Supported on Carbon for Methanol Electro-Oxidation

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**Abstract**— A series of Pt-Ni bi-metallic electro-catalysts supported on carbon (Pt-Ni/C) with varying content of Ni were synthesized by an organic precursor route. The metallic composition and crystal structure of these bi-metallic catalysts were determined by EDS and XRD. The size of the alloy particles and their distribution and appearance were examined by TEM. Methanol electro-oxidation activities of these catalysts were evaluated by preparing a porous gas diffusion electrode (PGDE) and performing cyclic voltammetry in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub>/1 M CH<sub>3</sub>OH medium. The specific activity, roughness factor and electrochemical surface area values obtained from CV analysis for Ni containing Pt electro-catalysts were more than Plain Pt electro-catalysts supported on carbon. The CV obtained in presence of methanol also showed that the Ni containing composition gives more predominant methanol oxidation peak than Pt alone electro-catalyst.

**Index Terms**— Cyclic voltammetry, Catalytic activity, Electro-catalysts, Fuel cell, Methanol, Nickel (Ni), Platinum (Pt), Porous gas diffusion electrode.

## 1 INTRODUCTION

Fuel cells are electrochemical device which converts available chemical energy directly into electrical energy with high efficiency. The efficiency of a fuel cell can be as high as 85% with cogeneration and can exceed depending upon the type of fuel used [1]. Hydrogen is preferred choice as a fuel in fuel cell being a simplest fuel to be oxidized electrochemically, but being gaseous in nature makes it difficult to store and transport necessitating to search for an alternative fuel which can easily be synthesized from it. Methanol is a suitable choice as a fuel for fuel cell, which carries several advantages over hydrogen, being cheap, high theoretical energy density, liquid in nature, easily handled, transported, stored and can distributed with existing infrastructure [2]. At present methanol is used in fuel cell by converting it into hydrogen by steam reforming process [3], but it is also possible to use methanol as a fuel instead of hydrogen. The fuel cell which uses methanol directly as a fuel is known as direct methanol fuel cell (DMFC). In the past decades, DMFC have attracted

fuel, high energy efficiency, low exhaustion and fast startup [4-6]. Although lot of progress has been made in the development of DMFC, however, two problems encountered are the slow methanol oxidation kinetics at anode in low temperature and methanol crossover from anode to cathode resulting short-circuiting the cell [7 - 8].

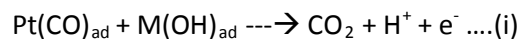
Oxidation of methanol over an electrode is multistep and sluggish reaction [9 - 11] that requires multiple sites of adsorption over a catalyst surface to dissociate C-H and C-O bonds. Therefore a catalyst capable to oxidize methanol electrochemically should have two types of active surface site, one which can dissociate C-H bond and other to desorb carbon monoxide (CO) by providing OH species. Pt is most preferred electro-catalyst for the methanol electro-oxidation, which can easily dissociate the C-H bonds, but easily poisoned by CO, which is the by-product of methanol oxidation. Therefore, to oxidize CO from the surface of Pt, Pt is alloyed with the oxophilic metals [12 - 13]. Oxophilic metals have OH species adsorbed on their surface, which is desorbed on reaction with CO forming CO<sub>2</sub> and H ion by binary mechanism. Several bi-metallic [14 - 19], tri-metallic [20 - 21] and multi-metallic [22] electro-catalyst has been studied taking this factor into account and reported enhanced activity with bi-, tri- and multi-metallic systems. The enhancement in catalytic activity is best explained by well known bi-functional mechanism, where CO

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extensive attention due to its advantages of low operating temperature (<100 °C), easy transportation and storage of

poisoned platinum is regenerated via a surface reaction between CO and oxygenated species formed on second metal associated with Pt, which can be well shown by following equation:



Nickel is recognized as a oxophilic metal and it forms oxygenated species such as NiO, Ni(OH)<sub>2</sub> and NiOOH. These species can donate OH species when required for oxidation of CO from Pt surface thus making the Pt surface free for further reaction. So the electrochemical oxidation of methanol is coupled chemical reaction, which requires two types of surfaces for completion. Such type of reactions can be well investigated by an electrochemical technique cyclic voltammetry.

Cyclic voltammetry is the most powerful technique to investigate coupled chemical reactions. In this method, the current is measured while the potential of working electrode is cycled at a fixed rate between two reversal points. The resulting plot of current versus potential is termed a cyclic voltammogram (CV). The CV is a complicated, time-dependent function of a large number of physical and chemical parameters and can provide information about kinetics and mechanism of electron transfer process [23 - 25]. It also offers a rapid location of redox potentials of the electro-active species, and convenient evaluation of the effect of media upon the redox process. It has already been used by some people for the kinetic study of electro-oxidation of methanol and evaluation of catalytic activities of fuel cell catalysts [26 - 27].

In this work, we have synthesized a series of Pt-Ni bimetallic alloyed catalysts supported on carbon (Pt-Ni/C) by an organic precursor route. In all composition the concentration of Ni is varied keeping the Pt concentration constant to understand the effect of Ni concentration in methanol electro-oxidation reaction. The compositions of all these electro-catalysts were confirmed by EDX (Energy Dispersive X-ray spectroscopy) and AAS (Atomic Absorption Spectroscopy) technique. Alloy formation between Pt and Ni was confirmed by XRD (X-ray Diffraction). The size of Pt-Ni alloy particles were determined by TEM, which were also compliance with result obtained from XRD. Electro-

catalytic activity for methanol electro-oxidation was then evaluated using cyclic voltammetry technique.

## 2 MATERIALS AND METHODS

### 2.1 Chemicals

All chemicals were of analytical grade and used as received. The hexachloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O) was used as a precursor compound for Pt. For synthesis of Nickel laurate, nickel chloride hexahydrate (NiCl<sub>2</sub>.6H<sub>2</sub>O) and Lauric acid was used. Other chemical reagents such as Ammonia, Methanol, Sulphuric acid used in this work were purchased from Merck India. Vulcan XC-72 with a BET surface area of about 240 m<sup>2</sup>g<sup>-1</sup> obtained from Cabot Corporation was used as a support for Pt and Pt-Ni electro-catalysts.

### 2.2 Synthesis of Nickel Laurate

0.01 Mole of Ni in the form of Nickel Chloride hexahydrate (2.376gm, NiCl<sub>2</sub>.6H<sub>2</sub>O) was dissolved in 200 ml of water and 4.0 g of Lauric acid dissolved in 100 ml of ammonium hydroxide solution. Then Lauric acid solution was added drop wise into Nickel Chloride solution under constant stirring at ambient temperature maintaining the pH of this solution to 6.5 using dilute hydrochloric acid. The total volume of the solution was made to 400 ml. The light green precipitate obtained was allowed to settle for one hour and filtered through Buckner funnel using Whatman No 42 paper. The light green precipitate obtained is Nickel laurate, which was washed 4 to 5 times with MilliQ water for any impurities and dried under vacuum over calcium chloride at ambient conditions for 48 hrs. The compound obtained was confirmed as nickel laurate by FT-IR (Fourier transform – Infra red) and UV-Vis (Ultra Violet – Visible) spectroscopic analysis. The amount of Nickel present was estimated by colorimetric analysis, which showed the ratio of Ni to Lauric acid is 2:1.

### 2.3 Synthesis of Pt/C and alloyed Pt-Ni/C Electro-catalyst

Pt/C electro-catalyst was prepared by adding 5.26 ml of neutralized hexachloroplatinic acid (38 mg/ml Pt) in 1.8 g of homogenized slurry of carbon black Vulcan XC 72. Pt in the form of hexachloroplatinic acid adsorbed on the surface of carbon was then reduced by diluted formaldehyde solution. The resulting suspension was then filtered,

washed copiously with hot MilliQ water and dried in an air oven at 110 °C. To synthesize Pt-Ni/C electro-catalyst, the above prepared Pt/C electro-catalyst was ultrasonically dispersed in ethanol until homogeneous slurry. Nickel laurate dissolved in ammoniacal ethanol was then added to this slurry to get the required concentration of Ni. This suspension was dried at 80 °C under constant stirring. The dry mass as obtained was pulverized and subjected to reduction and heat treatment. The reduction and heat treatment was carried out at 900 °C using a nitrogen – hydrogen gas mixture.

### 2.4 Porous Gas Diffusion Electrode Preparation

The porous gas diffusion electrode (PGDE) was prepared for each of the catalysts powder synthesized. For PGDE 281.25 mg of catalysts powder, corresponding to 0.5 mg Pt/cm<sup>2</sup> of electrode, was mixed with 1.9 ml of PTFE suspension (10 wt%) and agitated ultrasonically to form homogeneous slurry. 3 ml of propane-2-ol was added to this mixture as wetting agent and mechanically stirred to form a paste. The paste was then transferred on to a 7.5x7.5 cm area of hydrophobised porous carbon paper and hand rolled to get a uniform catalyst layer. The electrode thus obtained was dried at 120 °C, heat treated at 280 °C and then sintered at 340 °C.

### 2.5. Electro-catalyst Characterization

X-ray diffraction (XRD) pattern of these catalysts were recorded on Philips diffractometer (Model PW1710) using Cu K $\alpha$ 1 radiation ( $\lambda = 1.54060 \text{ \AA}$ ) source. The electro-catalyst powder was uniformly distributed in a quartz block and 2 $\theta$  Bragg angles were scanned over the range of 0 – 800 with a scan rate of 1 degree per minute. The EDX analysis for bulk composition of electro-catalysts were carried out under vacuum in an OXFORD LEO 1450 system at a generator tension of 20 kV. TEM (Transmission Electron Microscopy) was carried out using a Zeiss Make microscope model Libra® 120 that can operate with accelerating tensions up to 120 keV with a resolution of 0.23 nm. The grid used was a carbon film coated 300 mesh copper having a diameter of 3 mm.

### 2.6. Electrochemical Measurement

The Cyclic voltammetry measurements were carried out in a standard electrochemical cell in 0.5 M H<sub>2</sub>SO<sub>4</sub> as supporting electrolyte at ambient temperature, using computer controlled Autolab PGSTAT 30 (GPES version 4.7) potentiostat at a scan rate of 40 mV/s. Before the experiment the electrolyte was purged with nitrogen gas for 2 hour to remove traces of air/oxygen and during the experiment a gentle flow of nitrogen was maintained over the electrolyte surface. A PTFE (Polytetrafluoroethylene) coated graphite rod having a circular groove to hold PGDE was used as the working electrode. A platinum mesh was used as a counter electrode and reference electrode used was SHE (Standard Hydrogen Electrode).

## 3 RESULTS AND DISCUSSION

EDX analysis was carried out to determine the bulk composition of electro-catalyst. The composition obtained is shown in Table 1 and was found to be same as intended while preparation. EDX spectrum obtained for Pt/C and Pt-Ni/C are shown in Figure 1 and Figure 2 respectively, where the presence of Pt and Ni is clearly marked.

**Table 1:** Composition of Pt-Ni/C electro-catalysts obtained by EDX analysis

Nominal Composition of Pt-Ni/C Electro-catalysts	EDX Pt Content (Atom %)	EDX Ni Content (Atom %)
1:0.05	96	4
1:0.15	87	13
1:0.25	78	22
1:0.50	67	33
1:1	51	49

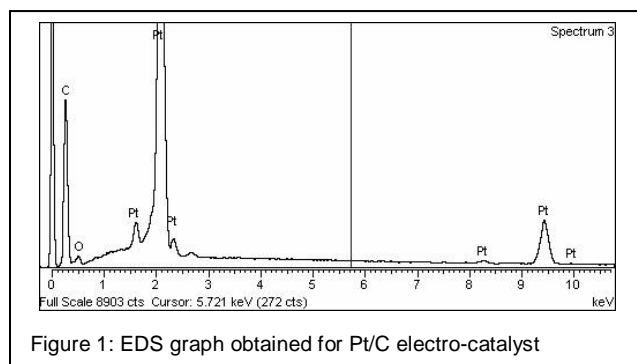
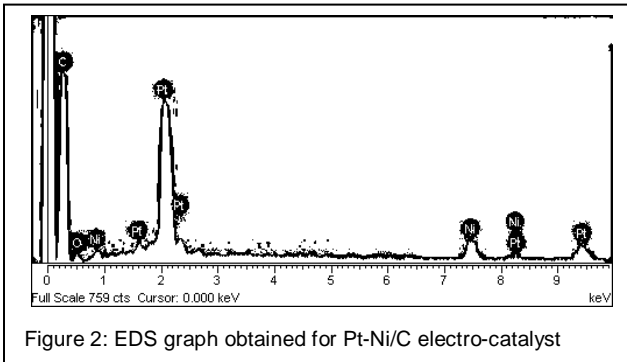
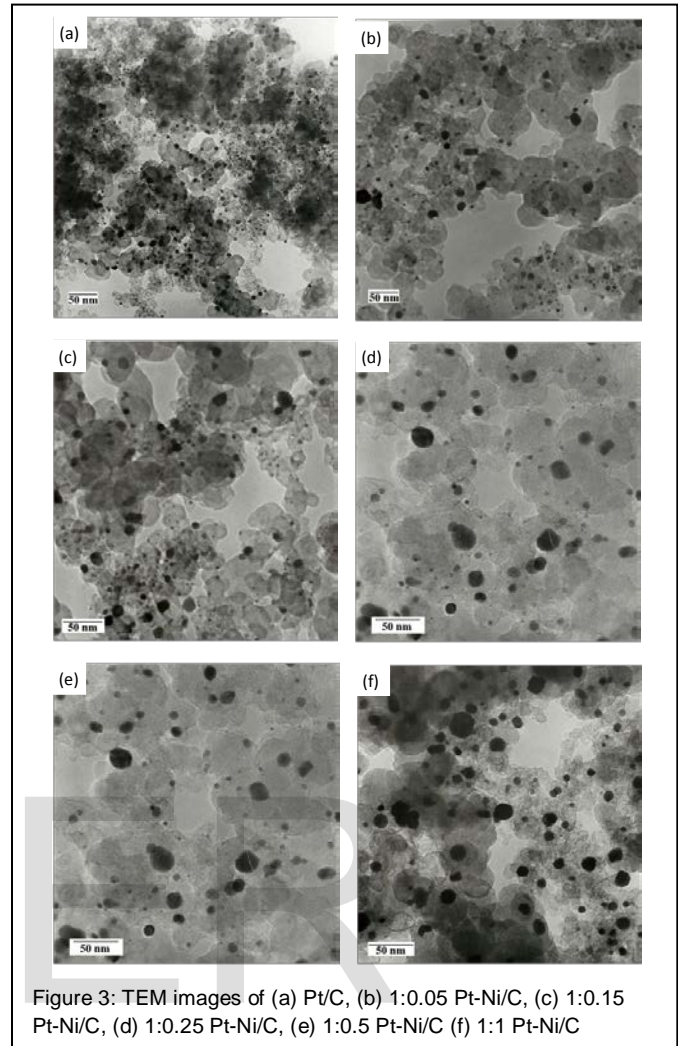


Figure 1: EDS graph obtained for Pt/C electro-catalyst



The size and distribution of Pt and Pt-Ni alloy nanoparticles on carbon surface was investigated by TEM. TEM Images obtained are shown in Figure 3 and it showed that the size of particles is in the range of approximately 8 – 12 nm, which is in good agreement with the XRD data. Figure 3 also showed that the size of particles increased with the concentration of Ni, it also showed that the alloy particles are distributed evenly without any agglomeration over the carbon surface.



The XRD pattern obtained for Pt/C and Pt-Ni/C electro-catalysts is shown in Figure 4, and their crystallographic parameters derived from their XRD data are summarized in Table 2. The diffraction peak at  $2\theta = 25^\circ$  observed in all the diffraction patterns of the carbon-supported catalysts is due to the (002) plane of the hexagonal structure of Vulcan XC-72 carbon.

**Table 2:** Crystallographic data obtained from XRD pattern of Pt/C and Pt-Ni/C electro-catalysts

Electro-catalysts	Crystallite size (nm)	Lattice Parameter
Pt/C	8.5	3.9191
1:0.05 Pt-Ni/C	9.2	3.8987
1:0.15 Pt-Ni/C	10.0	3.8964
1:0.25 Pt-Ni/C	10.5	3.8756
1:0.5 Pt-Ni/C	10.8	3.8323
1:1 Pt-Ni/C	11.0	3.8175

The peaks at about  $2\theta = 39.9, 47.5,$  and  $69.5$  is assigned to (111), (200) and (220) crystal plane of Pt, and could be fitted to a face-centered cubic (fcc) structure [28].

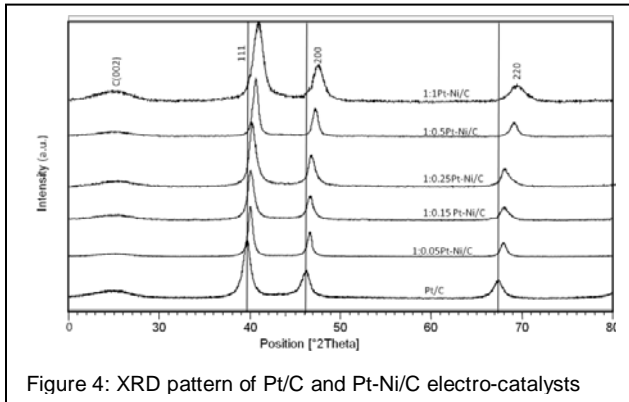


Figure 4: XRD pattern of Pt/C and Pt-Ni/C electro-catalysts

The absence of any peak corresponding to nickel and shift of Pt peak to higher theta value suggest that nickel is largely alloyed with platinum. It is also evident from figure 3 that with the increment of nickel content the XRD peak positions are shifted to higher theta value indicating that the alloying increases with the increasing content of nickel. The average particle size were obtained from the broadening of (111) diffraction peak in the XRD pattern of the Pt/C and Pt-Ni/C electro-catalysts, assuming spherical shape for the particles and using the Debye Scherrer equation [29]. The crystallite size found to be in the range of 8.5 to 11.0 nm, which is shown in Table 2. The growth of Pt crystallite size with increasing Ni content could be due to agglomeration of Ni with Pt resulting in the increased alloying of Ni with Pt. Table 2 also enlists lattice parameter value of Pt/C and Pt-Ni/C catalysts showing a linear drop in its value with increasing Ni content. This drop could be due to the incorporation of Ni in Pt lattice indicating that the extent of alloy formation increases with concentration of nickel.

The Pt/C and Pt-Ni/C electro-catalysts were analyzed in 0.5 M  $H_2SO_4$  and 0.5 M  $H_2SO_4$  / 1 M  $CH_3OH$  solution using voltammetry. Cyclic voltammograms (CV) of the electro-catalysts in 0.5 M  $H_2SO_4$  at ambient temperature was obtained during scanning between 0.0 and 1.2 V vs. SHE with a scan rate of 40 mV/s. The CV of both Pt/C and Pt-Ni/C electro-catalysts indicate the presence of polycrystalline Pt as shown in Figure 5. The peaks for the adsorption / de-

sorption of hydrogen and preoxidation / reduction on the Pt surface in  $H_2SO_4$  are clearly shown between 0.0 – 0.37 V. Proceeding further with the sweep of the potential it passes through a region, where only a weak and constant current is observed which signify only charging the capacity of the electrode double layer which lasts at about 0.6 V. At above 0.6 V, current rises and shows the formation of oxide at the surface of platinum [30 - 31]. CV obtained for these catalysts shows well defined Hydrogen adsorption/desorption peaks, however the height and area are increased with the concentration of nickel. Double layer and oxide formation region also showed similar trend, indicating that the formation of oxide in Pt-Ni/C are more pronounced than Pt/C, which is a good indication for methanol oxidation reaction. No characteristic features of Ni oxidation were found on continuous sweeping between these potentials.

The electrochemical surface area was evaluated from the CV by measuring the hydrogen desorption peak ( $A_p)_{des}$ , after subtracting the double layer capacitance and assuming monolayer adsorption charge of  $210 \mu C/cm^2$  for a smooth Pt electrode and using equation (2) [32 – 34].

$$S (cm^2) = \frac{(A_p)_{des} \mu C}{210 \mu C cm^{-2}} \dots\dots(2)$$

The roughness factor was calculated by using the following relation [35]:

$$Roughness\ Factor = \frac{Electrochemical\ Surface\ Area}{Apparent\ Surface\ Area} \dots\dots(3)$$

This relation shows that the value of roughness factor is equal to one when the real surface area of an electrode is exactly equal to its apparent surface area.

The Specific activity,  $A_0 (\mu A/cm^2)$ , defined as the current density per unit active electrode area ( $S_r$ ), was evaluated from current values at  $E = 900$  mV ( $i_{900}$ ), using the following equation [32 – 34]:

$$A_0 = \frac{i_{900} (\mu A)}{S_r (cm^2)} \dots\dots(4)$$

The data given in Table 3 show that the electrochemical surface area and roughness factor of all the Pt-Ni alloy composition is higher than Pt alone catalyst. The increase in these values could be attributed to presence of Ni, whose concentration was increased linearly for this series of catalysts.

**Table 3:** Specific activity, Electrochemical Surface area and Roughness factor values for Pt/C and Pt-Ni/C bimetallic alloyed electro-catalysts

Electro-catalysts	Specific Activity (mA/cm <sup>2</sup> )	Electrochemical Surface Area (m <sup>2</sup> /g)	Roughness Factor
Pt/C	0.106	31.94	160
1:0.05 Pt-Ni/C	0.131	35.23	175
1:0.15 Pt-Ni/C	0.141	36.87	185
1:0.25 Pt-Ni/C	0.150	39.94	200
1:0.5 Pt-Ni/C	0.220	42.89	215
1:1 Pt-Ni/C	0.191	43.21	216

Methanol oxidation current measured on the Pt-Ni/C based electro-catalysts in 1 M CH<sub>3</sub>OH in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at ambient temperature and at a scan rate of 40 mV/s exceeds that obtained with Pt/C. The comparison of the onset potential for methanol oxidation on Pt-Ni/C and Pt/C indicates that the Pt-Ni/C electro-catalysts show relatively good catalytic activity. Theoretically, methanol oxidation at Pt electrode surface may proceed at 0.046 V vs. SHE as shown by following equation:



Therefore, the lower onset potential indicates clear evidence for superior electro-catalytic activity for methanol electro-oxidation. As shown in Table 4, all of the Ni containing catalysts have lower onset potentials and higher current than Pt/C and 1:0.5 Pt-Ni/C showed lowest onset potential and highest current density. From Table 4, it is also clear that the methanol oxidizing current is increased with increasing content of Ni from 201 to 347 mA/mg of Pt. The CV for methanol oxidation at Pt/C and Pt-Ni/C are taken in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and 1 M CH<sub>3</sub>OH in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution is shown in Figure 5 and Figure 6 respectively, which confirms the data shown in the table 4.

**Table 4:** Onset potential and peak current values of methanol electro-oxidation in Pt/C and Pt-Ni/C electro-catalysts

Electro-catalysts	Onset Potential (V)	Peak Current (mA/mg Pt)
Pt/C	0.735	201
1:0.05 Pt-Ni/C	0.722	218
1:0.15 Pt-Ni/C	0.710	219
1:0.25 Pt-Ni/C	0.710	333
1:0.5 Pt-Ni/C	0.685	347
1:1 Pt-Ni/C	0.698	347

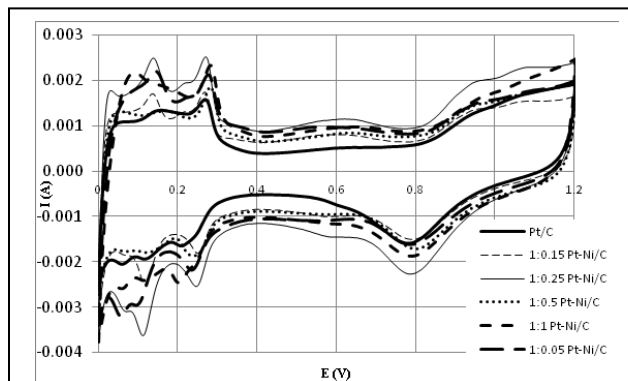


Figure 5: CV of Pt/C and Pt-Ni/C electro-catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 40 mV/s at ambient temperature

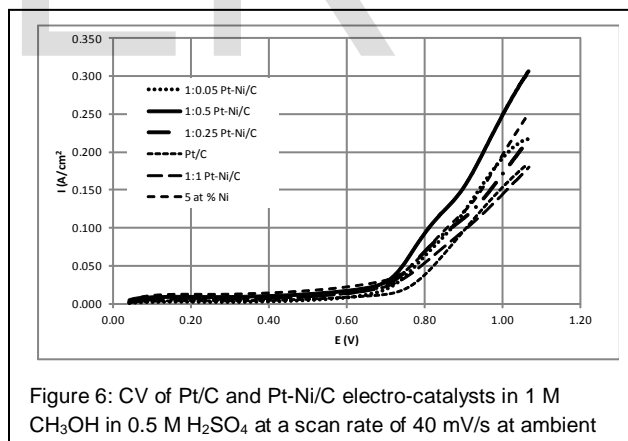


Figure 6: CV of Pt/C and Pt-Ni/C electro-catalysts in 1 M CH<sub>3</sub>OH in 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 40 mV/s at ambient

#### 4 CONCLUSION

Electro-catalytic activity of Pt-Ni/C electro-catalysts synthesized by using an organic precursor of Ni, reduced by hydrogen and heat treated at 900 °C, were investigated in respect of Pt/C by XRD, TEM and cyclic voltammetry technique. The XRD results showed alloy formation between Pt and Ni were gradually increased with concentration of Ni. TEM investigation showed even distribution of alloy particles on carbon black in the size range of 6 – 12 nm. CV

showed that Pt-Ni/C has better methanol oxidation activity than Pt alone catalyst. The maximum activity towards methanol oxidation is obtained for 1:0.5 Pt-Ni/C composition among all the catalyst combination studied in this work.

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