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Performance Evaluation of Nickle Platinum Novel Electrocatalysts for Proton Exchange Membrane Fuel Cell

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***Abstract*—**Among different types of fuel cells, the proton exchange membrane fuel cell (PEMFC) represents promising technology due to its lower operating temperature and higher efficiency. PEMFC can bring revolution in automobile industry by providing power to drive by consuming less fuel in a environmental friendly way. However, right now the main hurdle for its commercialization is the sluggish oxygen kinetics or slow reduction of oxygen at respective electrodes. To accelerate the sluggish oxygen reduction reaction (ORR) different types of expensive noble Pt alloys has been used as catalyst at cathode. The use of Pt based catalysts increases the cost of PEM fuel cell production therefore extensive research has been carried out to explore and develop different kinds of low costcatalysts as an alternative option. This study involves fabrication and testing of Ni-Pt ZIF as substitute electrocatalyst for cathode in PEM fuel cell. Ni-Pt has found to be a good substitute with a peak power density of 450 mW.cm^{-2} at temperature of 75℃ with Nickle to Platinum ratio of 9:1.

***Keywords*—** PEMFC, ORR, ZIF, Electrocatalyst

I. INTRODUCTION

Fuel Cells are electrochemical devices to convert chemical energy resulting from oxidation process to electrical energy [1]. Fuel Cells are highly efficient conversion devices with theoretical efficiency of 83%, however, typically their value ranges between 40-60 % [2]. Due to mechanical stability and zero emission power source, protom membrane fuel cell (PEMFC) is seeking much attention in recent years [3]. PEM fuel cell is one of the most efficient contestants for power hotspots and electric drive vehicles. PEM fuel cel is also known as polymer electrolyte membrane fuel cell is fabricated from proton-conducting polymer electrolyte membrane, usually a perflourinated sulfonic acid polymer [4]. On respective electrodes usually two types of chemical reactions which are also known as oxidation-reduction (redox) reactions take place.

Oxidation process occurs at anode in which hydrogen molecule loses its two conducting electrons that flows through outer circuit producing electric current. Reduction process takes place at cathode which is complex phenomena. Reduction reaction occurs in three modes in which either one, two or four electrons transfer takes place thus forming hydrogen oxide, hydrogen per oxide ions or water molecule. In order to have clean energy both of contributing elements (H_2 and O_2) should be pure so that the end product obtained is pure water with no environmental hazards. In order to have complete reaction usually the four electron pathway is desired to make water molecule [5]. Overall reactions are represented as under.

Reaction at anode

$$2H_2 \rightarrow 4H^+ + 4e^-$$

Cathode Reaction

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Overall Reaction

$$2H_2 + O_2 \rightarrow 2H_2O$$

The performance of PEM fuel cell is evaluated through the kinetics of electrocatalytic reactions that involves transfer of electrons from hydrogen to oxygen, which is also knows oxygen reduction reaction (ORR) [6]. The working of the PEMFC is presented in Fig. 1.

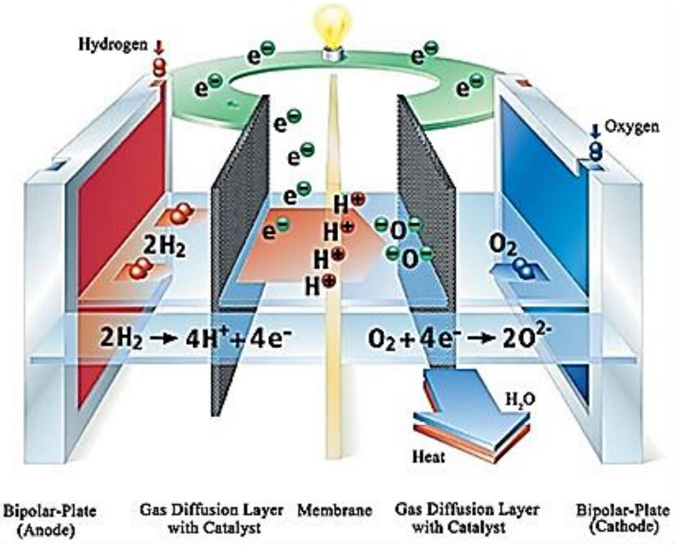

Fig.1 Schematic figure of PEMFC

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A. *Research Problem*

In commercialization of low temperature fuel cells such as PEM fuel cell, the primary need is to develop a highly porous material which is low cost, durable and highly active. To accelerate the sluggish oxygen reduction reaction (ORR) different types of noble Pt alloys has been used as catalyst at cathode which has adversely affected the electrochemical performance of fuel cells due to its high loading effects [7]. Under these circumstances extensive studies has been carried out to explore and develop non noble Pt less catalysts as an alternative option. Among them the most interested compounds that have been developed are Zeolitic imidazolate framework (ZIF) based electroatalysts. ZIF's are porous crystalline materials which forms a connection between inorganic metals and polymer crystalline materials. They are also known as porous coordination polymers (PCPs). ZIF's has gained interest in field of energy storages devices because of its unique porous structure which can store potential electrons and act as high power density materials, high surface area, organic-inorganic hybrid nature and versatility [8].

Both the anode and cathode electrodes consist of highly dispersed Pt-based catalysts loading on carbon support to promote the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR). The reaction rate of the HOR on Pt is sufficiently fast, therefore the required amount of Pt loading at the anode can be less than 0.05 $mg.cm^{-2}$. However, at the cathode, the sluggish reaction kinetics of the ORR requires a much higher Pt loading (~0.4 mg/cm2) to achieve appropriate fuel cell performance [9]. Pt-based precious metal catalysts still suffer from several critical problems, such as high cost, poor stability, crossover effect, and CO poisoning [10]. Reducing Pt loading or even completely replacing it with a low cost transition metal based catalyst without compromising the performance is a major challenge faced by the application of this promising technology.

B. *Research Objective*

The main hurdle in commercialization of PEM fuel cells are high cost of carbon supported Pt catalyst used in cathode which accounts for almost 60% of total fuel cell stack cost [11] and insufficient durability which occurs due to sluggish oxygen reduction reaction. Among existing fuel cell technologies PEMFC are most studied in recent years because of low working temperature, high power density and quick startup but problem is high cost of Platinum loading which are much required at cathode side for proper cell performance. Researchers and scientists around the world are trying to come up with new techniques to decrease the platinum loading like platinum nano-particles on carbon surface, or replacing the platinum group metal (PGM) with other metals like transition metals and alloys. This research is dedicated to study effect of transition metals such as Nickel based electrocatalyst and its combinations with low content PGM to achieve comparable performance with respect to Pt electrocatalysts alone.

II. METHODOLOGY

A. *Preparation of sample*

Nickle Platinum ZIF was prepared according to liturature [12]. According to this method 27.5g of 2-methylimidazole (2-MIM) was mas mixed in 100 ml of deionized (DI) water in one beaker with constant stirring while in another beaker 1.2 g of Nickel (II) nitrate hexahydrate which is a precursor of Nickle was dissolved in 15 ml of DI water . The solution was stirred contantly until green color was formed. Both of the solutions were mixed togetter under continuous stirrering for 6 hours at ambient temperature and pressure. After the complete reaction the solution was centrifuged three times while with mixing with fresh water to remove unreacted immadazole precipitate. After washing, the sample was dried overnight in oven at 80 ℃.

B. *Addition of Platinum*

Before pyrolysis of sample 10% of chloroplatinic acid (H_2PtCl_6) aas added to the dried sample . The sample yield was 500 mg in which 10 ml of H_2PtCl_6 solution was added.

C. *Pyrolysis*

After the addition of chloroplatinic acid, the sample was heated up at 350 ^{o}C for 1.5 h then the temperature is raised to 800 ^{o}C at a ramp rate of 5 ^{o}C per minute for 3.5 h in Helium and Argon atmosphere reflux. After preparing the black sample, it is cooled down to ambient temperature automatically. The sample was washed in 0.5M H_2SO_4 solution for 10 h. the catalyst which is prepared were accumulated by high centrifugation, recurrently cleaned with DI water and dehydrated at 100 ^{o}C under vacuum for 2-3 hour.Finally Ni-Pt ZIF was ready for testing. The final yield of the product was 100 mg. The block diagram of process is represented in Fig. 2.

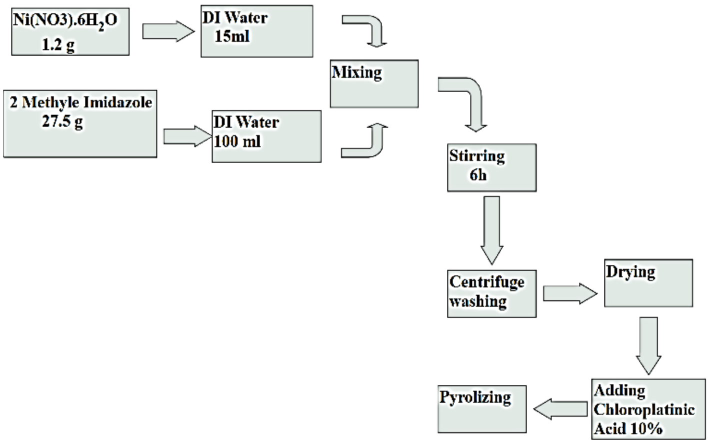

Fig.2 Block Diagram of Process

D. *Ink preparation*

In order to test our synthesized material it has to sprayed on nafion membrane to make membrane electrode assembly (MEA) out of it. In order to make ink of it 50mg of a Ni-Pt catalyst was mixed with 2.25ml of isopropyl alcohol and

0.3ml of nafion ionomer (20%wt). The ink was aggetated following by sonication of 10 mins for three time.

E. Membrane electrode assembly MEA)

MEA is a core component of a fuel cell which assists to produce electrochemical reaction that gives us free electron. MEA is made of polymer electrolyte membrane on which is sprayed on either side to make cathode and anode and this membrane is sandwich between two gas diffusion layers (GDL). GDL is typicaaly made of porous carbon fibers array. Its function is to create electrically conducting pathway for the collection of current. Loading on cathode side is typically higher then anode because the fuel (Hydrogen) passes through membrane and meet oxidant (Oxygen) at cathode side. In this research nafion membrane is used as polymer electrolyte membrane.

E.1. Material Loading

Area of material loading on nafion membrane is 1×1 $inch^2$. Weight of membrane before and after loading was recorded. As presented in table1 are the weights of MEA for pre and post weights of MEA before and after spray loading of catalyst.

Table 1. Loaded content

No	**Ni-Pt MEA**		
	Weight before loading (gm)	***After Anode Loading (gm)***	***After Cathode loading (gm)***
1	0.2559	0.2567	0.2617

F. Testing

Finally the product made was tested in a fuel cell test station which consist of an expandable research test cell and data acquisition center. The test cell consist of MEA slots with small openings in which hydrogen ($H_{2)}$ and oxygen ($O_{2)}$ gases or Air is supplied and silicon sheet with square opening in which MEA and GDL is placed all these components are sandwiched between bipolar anode and cathode plates. The purpose of silicon sheet is to insulate both plates so that short circuit won't occur. As shown in fig. 3 is complete model of a expandable research test fuel cell [13].

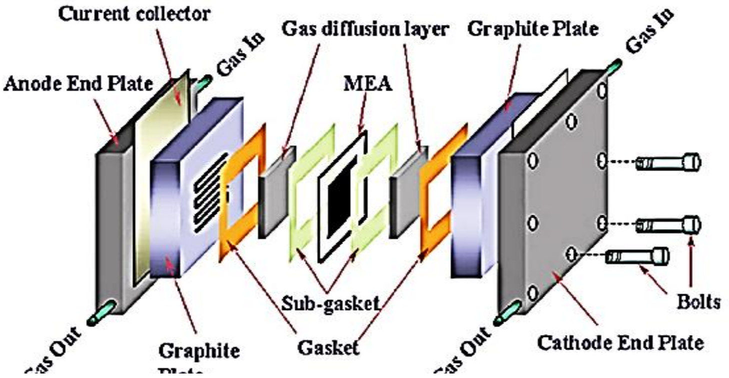

Fig.3 Expandable Research test fuel cell

III. RESULTS AND DISCUSSION

The oxygen reduction reaction (ORR) activities of Ni-Pt catalyst were evaluated through single MEA fuel cell test. In order to make it commercialized, it has to be tested under different parameters resembling the commercial fuel cell stack. In order to evaluate results first we tested MEA made of commercial platinum inside test station to check its performance parameters such as open circuit voltage (OCV), current density and peak power density [14]. Fig. 4 and 5 presents the polarization and power density graph of commercial standard platinum and nickel platinum respectively.

Fig. 4 shows us that commercial grade platinum has peak power density of 800 $mW.cm^{-2}$ at current density of 1800 $mA.cm^{-2}$ with OCV of 0.97 V. As the cell is connected to the external load it begins to draw current and subsequently power density increase until a point where concentration losses occur. The decrease in OCV is due to activation, ohmic and concentration losees occurs inside cell and circuit [15]. For a commercial grade platinum the slope will be always smooth as compare to other materials due to the presence of higher active sites [16]. Readings were taken at three different temperatures and in full humidified environment.

Fig.5 is polarization and power density curve for nickel platinum catalyst which shows almost same OCV of 0.975 V at current density of 16 $mW.cm^{-2}$. The peak power obtain for this catalyst is 450 $mW.cm^{-2}$ at temperature of 75℃ at current density of 850 $mA.cm^{-2}$ which is almost half as compare to commercial Platinum. A limiting current of 1400 $mA.cm^{-2}$ has been recorded for this catalyst.

The governing equtions for calculating Power is given by [16].

$$P = \frac{V_b^2 RL}{(Rint + RL)^2} \qquad (1)$$

V_b = fuel cell battery voltage (V)

Rint = effective internal resistance of a fuel cell (Ω)

R*L* = load resistance (Ω)

Open Circuit voltage OCV of fuel cell is calculated through Nerst Equation [17].

$$E = E^{\circ} - \frac{RT}{nF} lnQ_C \qquad (2)$$

s

E = cell potential (V) under specific conditions

E°= cell potential at standard conditions

R = ideal gas constant = 8.314 J/mol-K

T = temperature in (kelvin)

n = number of moles of electrons transferred

F = Faraday's constant = 95,484.56 C/mol

lnQ_c = the natural log of the reaction quotient

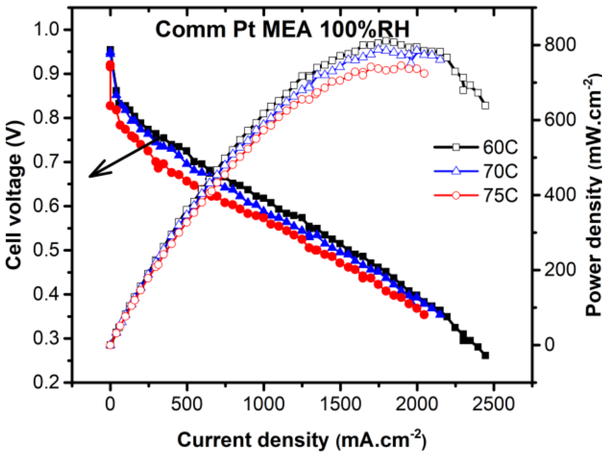

Fig. 4 The single fuel cell current-voltage polarizations curve. Test conditions: Nafion membrane, Catalyst =comm Pt/C cathode loading ~ 0.7 mg cm^{-2}, anode loading 0.5 mg cm^{-2}, cell area = 1×1 inch^2, T = 60℃,70℃,75 ℃ PO_2 = PH_2 = 1.0 bar, 100% Relative humidity.

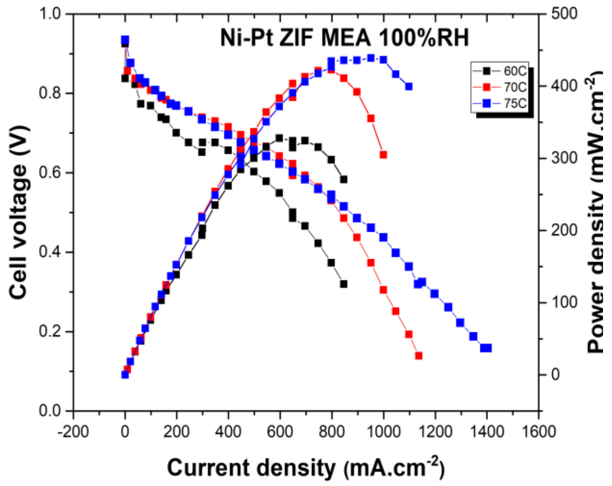

Fig. 5 The single fuel cell current-voltage polarizations curve. Test conditions: Nafion membrane, Catalyst = Ni-Pt , comm Pt/C cathode loading ~ 5 mg.cm^{-2}, anode comm Pt/C loading 0.8 mg.cm^{-2}, cell area = 1×1 inch^2, T = 60 ℃,70 ℃, 75 ℃ PO_2 = PH_2 = 1.0 bar, 100% Relative humidity.

Comparing both values of Fig. 4 and Fig. 5, we found that by reducing the amount of platinum in our catalyst from 90% to 10% has only reduced the peak power density by 40% while keeping the OCV constant. from Our investigation finds out that the reduction in peak power of catalyst as compare to commercial platinum is due to the limitation of active sites in this catalyst. The ORR activity mainly depends on the number of free electrons present on the surface area of the catalys which is called active sites. The reduction in cost of catalyst is significant as compare to the total power density drop.

IV. CONCLUSION

In summary Nickel (ii) nitrate hexahydrate has been successfully use as precursor to synthesized Ni-Pt ZIF. The well designed Ni-Pt ZIF with control structure morphology has been synthesized with control parameters which has shown much better electrochemical performance as compare to other metal ZIF's being synthesized. The reduction in cost of this catalyst as compare to commercial platinum is very significant relative to the peak powers. The performance parameters of this catalyst can be enhanced by the addition of other transition metals which subsequently can create more active sites thus facilitating ORR activity.

We believe that the proposed methodology will open up another road for the structure and blend of ZIF-based models, which will expand the broad utilizations of ZIFs; what's more, the as acquired Ni-Pt ZIF-based nanostructures will be magnificent materials for different applications such as catalysts, sensors and energy storage and conversion devices.

V. ACKNOWLEDGMENT

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