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Effect of Synthesis Procedures on Physical and Electrochemical Properties of Carbon Supported Pt/Ru Nanophase Electrocatalyst for Fuel Cell Applications

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The carbon supported Pt/Ru is found be most commercially used anodic electrocatalyst for direct methanol fuel cell applications however, there are ternary and quaternary metallic based catalyst also available. Here we report in outcome of the synthetic procedures on properties of carbon supported Pt/Ru catalysts. Different electrocatalysts were synthesized by using propylene glycol, ethylene glycol, glycerin, polyvynilpyrrolidone (PVP) ethylene glycol methodology, hydrazine, sodium borohydride, formic acid, sodium formate as reducing agents and electrochemical reduction of metals on carbon supported electrode. The synthesized electrocatalysts were characterized by; powder XRD, electron microscopic techniques like SEM, EDS, and TEM, Brunauer-Emmett-Teller (BET) for surface area analysis, and finally electrochemical discharge testing (EDT) was carried out to examine performance and durability of synthesized electrocatalyst (open circuit and on load voltages, current density and power density). The synthesized catalysts had shown high catalytic activity and CO tolerance in direct methanol fuel cell applications, higher activity is achieved by those electrocatalysts which are synthesized by using weak reducing agents as examined by electrochemical discharge testing methodology.

Keywords: Direct Methanol Fuel Cell, Pt-Ru electrocatalyst, Carbon black, Electrochemical Discharge Testing

1. INTRODUCTION

Today world is facing challenges of energy shortage and environmental pollution. Energy demand is growing rapidly. The increased demand is largely met by reserves of fossil, which have

manifold problems like environmental concerns and diminishing reservoirs [1]. Fuel cell technology is an excellent means to address all these issues. It is environmentally safe and gives high efficiency and reliability. Fuel cells have diverse applications like stationary power, transportation and portable electronics [2-3]. Fuel cells are classified on the basis of electrolyte membrane used like alkaline fuel cell (AFC), Phosphoric acid fuel cell (PAFC) and Polymer electrolyte fuel cell (PEM). Among these PEM fuel cell is mostly used for portable applications. The noble metal catalyst mostly used in PEM fuel cells is platinum, which is very expensive. This issue can be resolved by decreasing the platinum loading. Another challenge to PEM Fuel cells, especial alcohols based fuel cells, is CO poisoning of the catalyst. This issue is largely resolved by alloying a second metal which can oxidize CO to CO_2 and thus protecting catalyst from poisoning [4-5]. Various metals have been reported to oxidize CO to CO_2 like Ruthenium [6-7], Iridium [8] and Tin [9] etc.

In past decade, Pt-based bimetallic catalysts attracted many researchers [10]. Among them, carbon supported Pt/Ru nanoparticles catalysts are found to be of great interest since carbon supported Pt/Ru nanoparticles catalysts found to have resistance against CO poisoning and considered to be the most significant electrocatalyst for PEM fuel cells [11]. Particle size and surface area of the noble metals and their dispersion are the main parameters affecting the catalyst properties. These properties mainly depend upon the synthesis procedure. Variety of synthesis routes are reported for the synthesis of various catalysts like Polyol method [12], Colloidal method [13], Impregnation method [14], Thin film method [15], Electrodeposition method [16], Sputter deposition method [17], Bönnemanns' method [18], Pechini-Adams's method [19], Sol-gel method [20]. Among these, impregnation-reduction method is widely used for the synthesis of the electrocatalyst on carbon support. Different reducing agents are reported in the literature like Ethylene Glycol [21], Formic acid, Sodium Borohydride [22] etc. These reducing agents are used for different catalysts so it is difficult to deduce the best reducing agent. The aim of this study was to fabricate nanophase carbon supported Pt/Ru electrocatalyst by using different reducing agents in order to optimize the best suitable conditions. The optimization can be deduced based on the physical properties and electrochemical discharge testing outcomes.

2. EXPERIMENTAL

All chemicals were of analytical grade. Deionized water was used throughout the experiments. Acetylene black with average particle size 100 nm was used as carbon support. Acetylene black was treated with 30 ml H_2O_2 at 80 ºC for 24 Hours to create surface active groups [23].

2.1. Synthesis procedure

$PtCl_4$ and $RuCl_3$ were dissolved in 20-30 ml of appropriate solvent with gentle stirring at 80 ºC. The amounts of the metal salts were adjusted to get 5% PtRu/C catalyst with Pt:Ru atomic ratio 1:1. Acetylene black carbon was dispersed separately in 20 ml solvent for 30 minutes. Metal salts solution was added drop by drop to the carbon dispersion with vigorous stirring. The pH of the solution was

then raised to 11 with 1 M NaOH solution and reducing agent was then added to the solution (no need in case of polyol method where solvent acts as reducing agent) and temperature was raised gradually to 100 ^{o}C (170 ^{o}C in case of polyol method) in Paraffin oil bath. The molar ratio of the reducing agent and metal salts was kept 5:1. Temperature was maintained for 2 hours and then the prepared catalyst was filtered and washed with De-ionized water until neural. The resulting slurry was dried in vacuum oven at 80-90 ^{o}C to remove solvent contents.

Table 1. Summary of the Reducing agents, sample code, solvent used.

S No	Reducing agent	Sample code	Solvent	Concentration
01	Propylene Glycol	BG-1	N/A	>99.9%
02	Glycerin	BG-2	N/A	>99.9%
03	Hydrazine	BG-3	Water	65%
04	Sodium Borohydride	BG-4	Water	5%
05	Formic acid	BG-5	Water	85%
06	Sodium Formate	BG-6	Water	30%
07	Hydrogen	BG-7	N/A	N/A
08	Electrochemical reduction	BG-8	N/A	N/A
09	Ethylene Glycol	C-3	N/A	>99.9%

2.3 Physico-Chemical Characterization of PtRu/C catalyst

The synthesized catalysts were characterized PXRD, SEM, EDS, BET, TEM and catalyst testing is being by using Electrochemical Discharge testing (EDT) method.

2.4 Electrochemical characterization of the PtRu/C catalysts

The electrochemical measurements were performed on Our Laboratory made single cell with Electronic load and Fluke Digital multimeter. Nafion 115 was used as the polymer membrane. It was boiled first in water for 2 hours and then in 3% hydrogen peroxide for 2 hours to oxidize organic impurities followed by washing with distilled water. Treated membrane was boiled in 0.5 M sulfuric acid for 1hour and washed with distilled water.

Catalyst ink was prepared by suspending 100 mg of the synthesized catalyst in 10-20 ml of 10-20% isopropanol and water followed by 5 ml addition of 5% alcoholic nafion solution. The ink was allowed to sonicat at 60 ºC for 4 hours. 1 ml of the ink was applied on gas diffusion layer and dried at 80 ºC.

2.5 Membrane electrode assembly (MEA) preparation

The MEA was prepared by pressing the anode, carbon cloth (gas diffusion layer coated with catalyst ink), Nafion 117, carbon cloth (gas diffusion layer coated with catalyst ink) and cathode at 140

psi (10 barr) and 130 ºC for 2 minutes. Electrochemical Discharge testing (EDT) was performed by introducing 2 M CH_3OH solution in Membrane electrode assembly (MEA) to find out open circuit voltage, onload voltage, current density, power density and stability of the synthesized electrocatalysts [24].

Nine different carbon supported Pt/Ru nanophase electrocatalysts were synthesized by using propylene glycol (BG-1), glycerin (BG-2), hydrazine (BG-3), sodium borohydride (BG-4), formic acid (BG-5), sodium formate (BG-6), hydrogen reduction (BG-7), ethylene glycol (C-3) as reducing agents and electrochemical reduction of metals on carbon supported electrode (BG-8). The synthesized catalysts were characterized by PXRD, SEM, EDS, BET, TEM and Electrochemical Discharge testing (EDT). The comparative studies of the synthesized catalysts were carried out as their application in fuel cell.

3. RESULTS AND DISCUSSION

3.1. Powder X-ray Diffraction (PXRD)

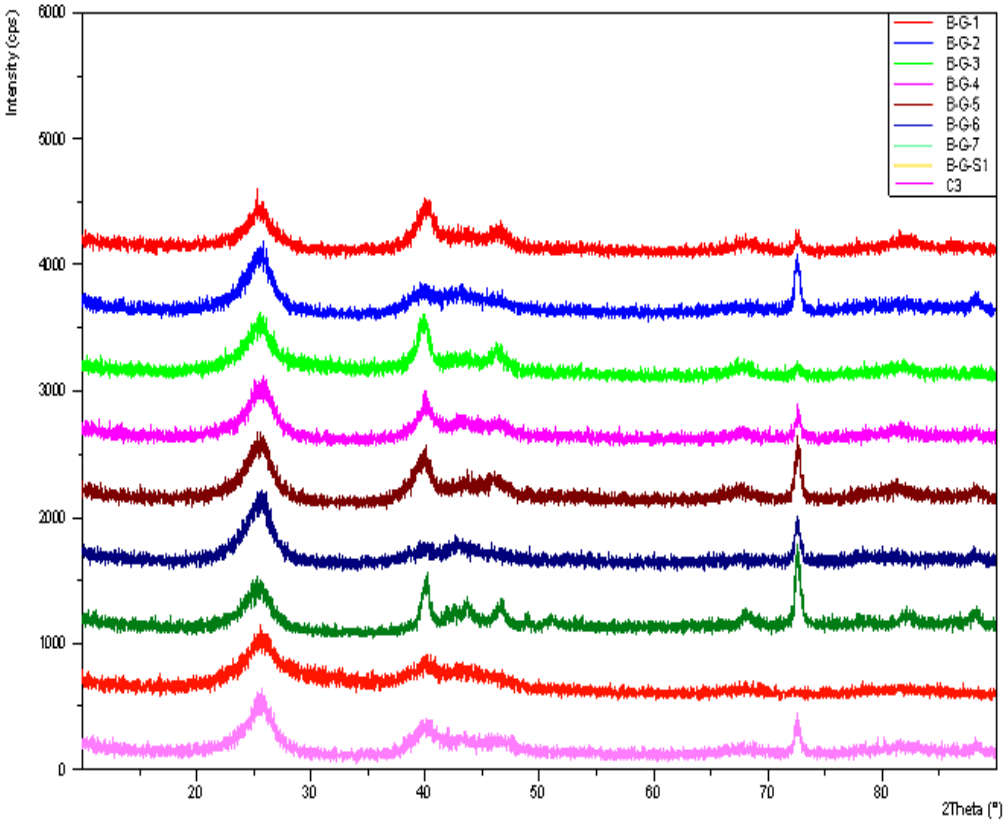

Figure 1. Combined PXRD pattern of synthesized 5% PtRu/C electrocatalysts

The PXRD technique was used to insight crystal structure, alloying of Pt-Ru and crystallite size. XRD patterns of support, individual metal reduced i.e. Pt and Ru, combined spectra of separately reduced Pt and Ru metal and carbon supported Pt/Ru nanocatalysts are shown in Figure 1. Diffraction

peak at 23-27 (2θ value) is due to carbon support which can be assigned to the hexagonal graphite structure(002) of the carbon and reflect its graphite degree [24]. All prepared Pt-Ru/C catalysts showed characteristic diffraction pattern of the Pt FCC crystal structure. Peaks were slightly shifted to higher values due to alloying of the Ru atoms into the FCC crystal structure of the Platinum [25]. Shift in the diffraction values were different for different synthesis routes indicating different amount of alloying of the Ru into Pt crystal structure. The broadness of peaks indicated the nanostructure of the prepared PtRu alloy. Crystallite size was calculated from the broadening of Pt(220) diffraction peak at 70 to 74 (2θ) . Different crystallite sizes were observed for various catalysts based upon their synthesis routes. Scherer equation was used to calculate the crystallite size.

$d = 0.9 \lambda \times 57.3 / (\beta \cos\theta_{max})$

Where, d = crystallite size, λ = wavelength (Cu-Kα, λ = 1.5406 Å), θ_{max} = half the angle of diffraction (2θ) and β = radians (peak-width at half peak-height).

Table 2. Average crystallite size of the 5% PtRu/C electrocatalysts calculated by Scherer equation

S.No	Sample	Reducing agent	Average crystallite size (nm)
1.	BG-1	Propylene glycol	7.80
2.	BG-2	Glycerine	12.39
3.	BG-3	Hydrazine	10.77
4.	BG-4	Sodium borohydride	13.65
5.	BG-5	Formic acid	9.19
6.	BG-6	Sodium formate	10.15
7.	BG-7	Hydrogen	14.28
8.	BG-8	Electrochemical reduction	8.96
9.	C-3	Ethylene Glycol	8.04

The X-ray Diffraction (XRD) results of the synthesized catalysts revealed crystallite size depends upon the reducing agent used. Catalysts synthesized using propylene glycol, ethylene glycol and formic acid had shown smaller crystallite size as compared to others. This can be attributed to the weak reducing power of these reducing agents which results in controlled reduction and thus smaller particle size and better distribution can be achieved.

3.2. Scanning Electron Microscopy (SEM)

The SEM analysis was used to check morphology and particle size of the synthesized catalyst supports. Carbon particles have different morphology and particle size depending upon the nature of the carbon used and in this research work Acetylene black (AB) was used as carbon support for the

electrocatalyst. The Scanning Electron Microscopy (SEM) images of the synthesized catalysts were taken which showed that particles of Acetylene black carbon were homogeneously distributed and of same size. The morphology of Acetylene black carbon was particle in nature having average particle size of 0.12 μm as shown in Figure 2.

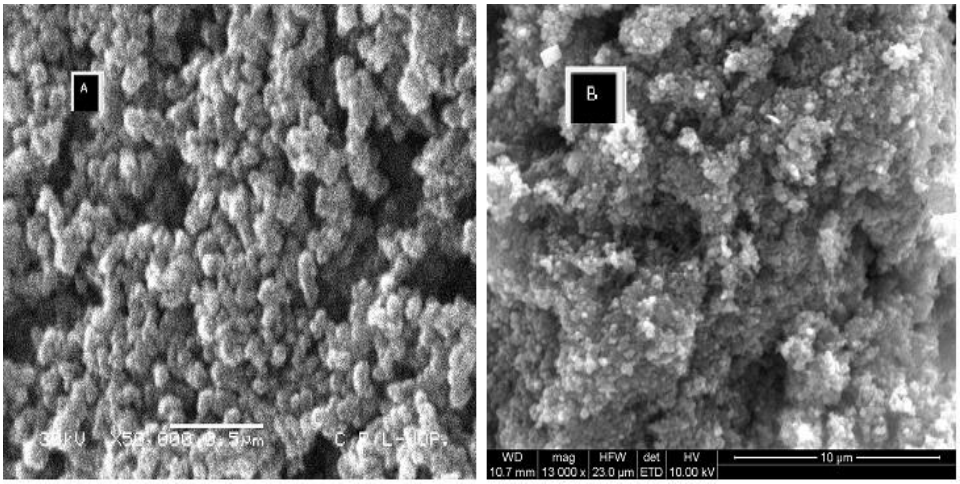

Figure 2. SEM image of carbon support (treated with 30 ml H_2O_2 at 80 ºC for 24 Hours) A= 0.5μm Bar, B = 10μm Bar.

3.3. Energy Dispersive Spectroscopy (EDS)

The EDS analytical technique was used to find percent metal composition and Pt/Ru alloy ratio of the synthesized carbon supported Pt/Ru nanocatalysts [26]. An attempt was made to prepare 2.5% loading of each metal in 1:1 ratio. Synthesized catalysts had shown different loadings and ratio depending upon the synthetic procedures used. Weak reducing agents had produced catalysts with good loading and Pt/Ru alloy ratio. The percent metal composition and Pt/Ru alloy ratio of synthesized catalysts are shown in Table 3.

Table 3. Metal composition and alloy ratio of 5% Pt/Ru on carbon support calculated by EDS analysis.

Sample code	Reducing agent	% Pt	% Ru	% C	Pt/Ru ratio
BG-1	Propylene Glycol	2.39	2.26	94.94	1.05:1
BG-2	Glycerol	2.42	2.31	94.80	1.04:1
BG-3	Hydrazine	2.37	2.01	94.86	1.17:1
BG-4	Sodium borohydride	2.35	2.19	95.25	1.07:1
BG-5	Formic acid	2.47	2.41	95.02	1.02:1
BG-6	Sodium formate	2.43	2.17	94.69	1.11:1
BG-7	Hydrogen	2.41	1.79	95.37	1.34:1
C-3	Ethylene Glycol	2.33	2.07	94.93	1.12:1

The EDS results of the synthesized catalysts showed that both Pt and Ru metals were reduced by using different reducing agents. The Energy Dispersive Spectroscopy (EDS) results indicated that the synthesized catalysts had different % metal compositions and Pt/Ru alloy ratio. Catalysts synthesized by using week reducing agents such as propylene glycol, glycerol and formic acid had shown % metal composition and Pt/Ru alloy ratio very close to actual values. The best results were given by Formic acid with Pt/Ru alloy ratio 1.02:1.

3.4 Brunauer-Emmett-Teller (BET)

The BET surface area technique was used to determine surface area of the acetylene black. The average surface area calculated by BET analysis for untreated acetylene black, treated acetylene black and catalyst.. There is a decrease in the BET surface area when carbon black is treated with hydrogen peroxide. This may be due to the blocking of pores by the surface groups created during the oxidation of the carbon with hydrogen peroxide as reported by Marcelo et.al. [25]. Surface area is further after the deposition of the Pt-Ru alloy nano particles on the catalyst support. This might be due to the filling of the pores in the acetylene black. The decrease is not very significant which suggest that most of the Pt-Ru alloy nanoparticles are adsorbed on the surface.

3.5. Transmission Electron Microscopy (TEM)

The TEM analysis was used to find out the average particle size, the particle size distribution and morphology of the Pt/Ru nanoparticles. TEM images of the various synthesized catalysts, at the carbon support was visible in the TEM micrographs in each case as large dark grey particles of average 120 nm with the small black Pt particles and dark brown Ru particles distributed upon the AB carbon support. The Pt/Ru nanoparticles were well dispersed with almost same particle size and shape in each case. The average particle size observed by TEM micrograph and XRD pattern is listed in below Table 4.

Table 4. Comparative average size measurement of 5% PtRu/C electrocatalyst by TEM and PXRD.

Sample code	Reducing agent	Average particle size by TEM (nm)	Average particle size by XRD (nm)
BG-1	Propylene glycol	6-8	7.80
BG-3	Hydrazine	--	10.77
BG-4	Sodium borohydride	10-12	13.65
BG-5	Formic acid	--	9.19
BG-6	Sodium formate	8-10	10.15
C3	Ethylene glycol	7-9	8.04

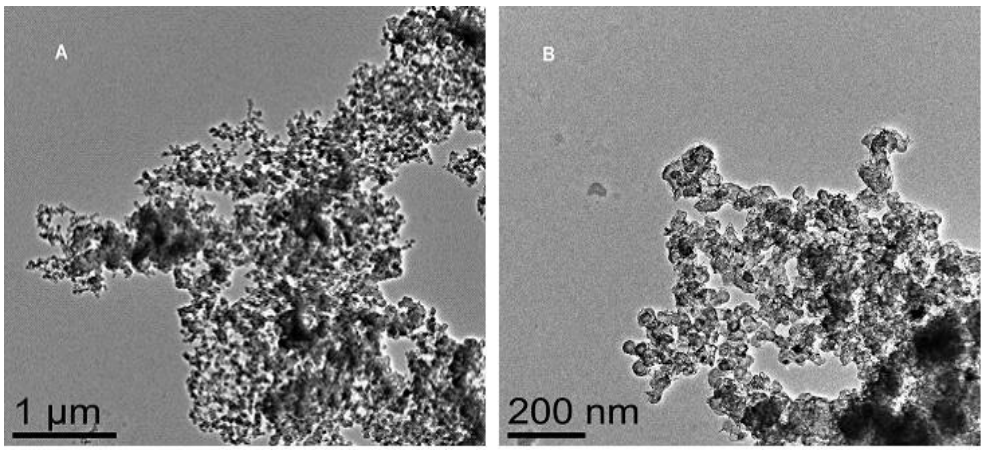

Figure 3. TEM micrographs of carbon support A) 1µm B) 200nm Scale

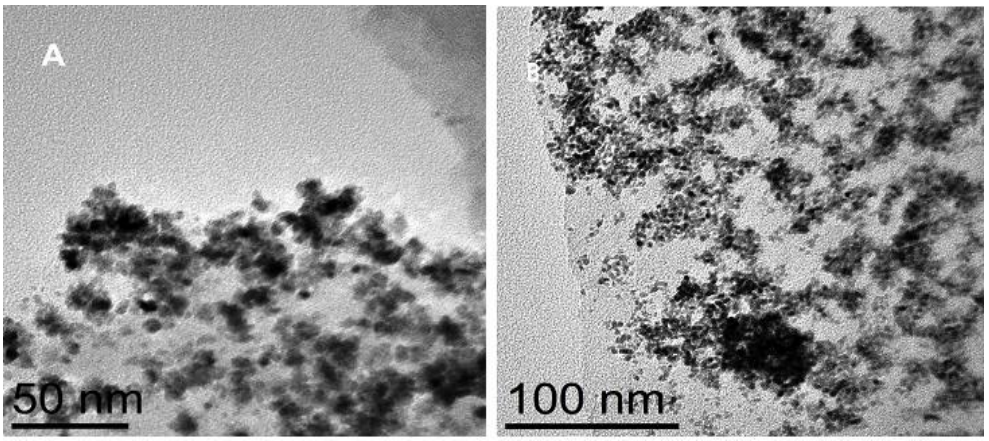

Figure 4. TEM micrograph of 5% PtRu/C nanophase electrocatalyst A) BG-1 at 50 nm B) BG-1 at 50 nm

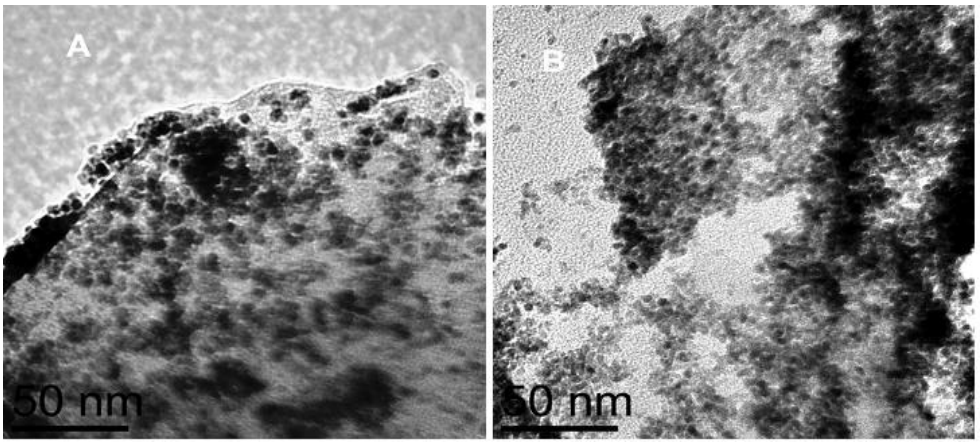

Figure 5. TEM micrograph of 5% PtRu/C nanophase electrocatalyst A) BG-3 B) C3

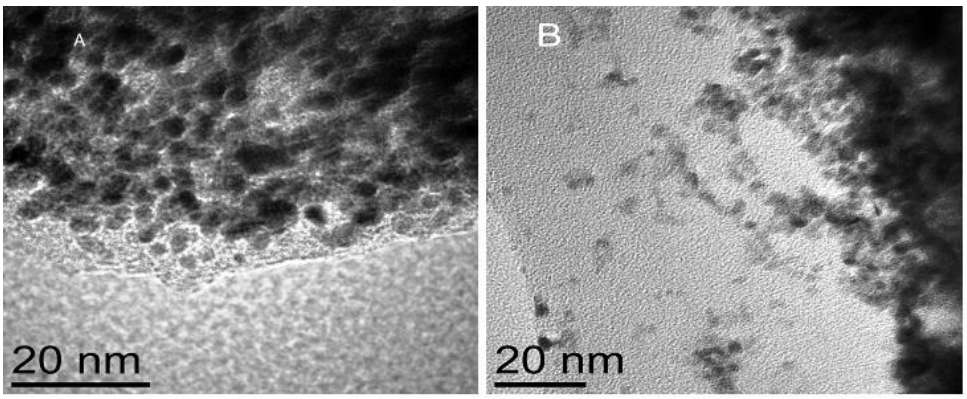

Figure 6. TEM micrograph of 5% PtRu/C nanophase electrocatalyst A) BG-5 B) BG-6

3.6. Electric Discharge behavior of the synthesized catalysts

It was observed that the synthesized catalysts had shown different electrochemical properties depending upon the synthetic method used. The synthesized catalysts having smaller crystallite size exhibited high electrochemical performances. The electrochemical performance of the synthesized catalyst is shown in Table 5

Table 5. Electrochemical performances of the synthesized 5% PtRu/C nanophase electrocatalyst, applied to Membrane Electrode Assembly (MEA)

Sample code	Reducing agents	Open circuit voltage (V)	Current density (mA/cm^2)	Power density (mW/cm^2)
BG-1	Propylene glycol	0.80	250	59.5
BG-2	Glycerol	0.79	220	49.2
BG-3	Hydrazine	0.78	240	49.6
BG-4	Sodium borohydride	0.78	200	42
BG-6	Sodium formate	0.80	250	49.6
BG-7	Hydrogen	0.75	180	37.7
BG-8	Electrochemical reduction	0.82	160	44
C-3	Ethylene glycol	0.80	200	41

The Electrochemical Discharge testing (EDT) results of the synthesized catalysts showed that catalysts synthesized by using propylene glycol, ethylene glycol, sodium formate had good open circuit voltage as compared to others but the catalyst synthesized by electrochemical reduction had shown the highest open circuit voltage i.e. 0.82 V. The lowest open circuit voltage was shown by the catalyst, synthesized by the direct hydrogen reduction i.e. 0.75 V. The open circuit voltage comparison of the synthesized carbon supported Pt/Ru nanocatalyst in shown in Figure 3.35.

The synthesized catalysts had shown variable current density. Catalysts synthesized by using propylene glycol and sodium formate had shown the highest current density i.e. $250mA/cm^2$ and the

catalyst synthesized by electrochemical reduction method had produced lowest current density i.e. 160 mA/cm^2 where as the highest power density was achieved by the catalyst, synthesized by using propylene glycol i.e. 59.5 mW/cm^2 and lowest power density was produced by the catalyst, synthesized by direct hydrogen reduction method i.e. 37.7 mW/cm^2. These all results showed that different synthetic methods used had shown different electrochemical properties. The values of current density at different onload potentials were measured and then the values of voltage (V) were plotted against the current density (10 x mA/cm^2) produced. The power density (mw/cm^2) of the synthesized catalysts was measured at different onload voltages by multiplying the current density produced and onload voltage.

4. CONCLUSION

Synthesized catalysts had shown different physical and electrochemical properties depending upon the reducing agents used. Weak reducing agents had produced catalysts with smaller particle size. Catalyst with the smallest particle size was synthesized by using propylene glycol i.e. 6-8 nm (calculated by TEM micrograph). Average particle size of the AB carbon support was calculated by SEM analysis i.e. 0.12 µm. EDS analysis had shown that catalyst synthesized by using formic acid produced high % metal deposition and good Pt/Ru metal alloy ratio i.e. 1.02:1. Catalyst with smaller particle size exhibited high electrochemical performance. Catalysts synthesized by using propylene glycol and sodium formate had shown good open circuit voltage and current density. Catalyst synthesized by electrochemical reduction method had shown highest open circuit voltage but low current density which is due to larger particle size. Catalyst synthesized by using propylene glycol had shown highest power density i.e. 59.5 mW/cm^2. Stability of the carbon supported Pt/Ru nanocatalyst was compared with carbon supported Pt nanocatalyst at various loads and also at current density of 25 mA/cm^2 as a function of discharge time. It had been observed that carbon supported Pt/Ru nanocatalyst had produced high current density and power density and also showed high discharge time as compared to carbon supported Pt nanocatalyst.

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