



### Research Article

## Influences of supporting materials for Pt-Ru binary catalyst in Ethanol fuel cell

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### Abstract

In the present work, Pt–Ru/OMP Pt–Ru/CX, and Pt–Ru/Vulcan electrocatalysts with different atomic ratios were prepared by sodium borohydride reduction method. The synthesized electrocatalysts physical characterization showed high particle dispersion on to the carbon supports and alloying degree. The prepared catalysts had different particle morphology, and their particle sizes were 2-4 nm. Electrochemical characterization of cyclic voltammetry and chronoamperometry were performed to study their activity toward carbon monoxide and ethanol oxidation. The electrochemical results obtained at room temperature showed that the Pt–Ru/CX and Pt–Ru/OMP carbon support catalysts demonstrated better catalytic activity for ethanol oxidation compared with the Pt–Ru/Vulcan carbon support catalyst. The superior performance of Pt–Ru electrocatalysts supported on carbon nanomaterial is the best electrical conductivity, and high electrochemical surface area.

**Keywords:** Platinum; Ruthenium; Carbon Xerogel; Ordered Mesoporous Carbon; Ethanol; Perborate.

### Introduction

The nature of the support is very essential to establish the distribution and stability of the metal crystallites, the electronic properties of the metal including metal support interactions and the amount of alloying in bimetallic catalysts, mass move confrontation and the ohmic resistance of the catalyst surface (Figueiredo et al., 2006; Calvillo et al., 2009; Moliner et al., 2008; Li et al., 2006). Carbon is the best support material for the metal catalyst preparation. Vulcan carbon black is the most used catalyst support; it is have high catalytic activity and excellent chemical stability. Nevertheless Vulcan carbon contains primary pores very less adding of the metal catalyst not properly incorporated to the carbon support. Additionally found that impurities present in the Vulcan surface destabilize the catalyst and catalytic performance (Jang et al., 2011; Zhang et al., 2013; Chengwei Zhang et al., 2014).

In this context carbon xerogels are attracting much attention for their unique and controllable properties, such as high surface area, mesopore structure with narrow pore size distribution, and high purity. Most of the research work denote as Carbon xerogels are prepared the polycondensation of resorcinol with formaldehyde carried out by thermal and drying method.

Ordered mesoporous carbon is another useful support material for preparation of the metal catalyst. It is also received growing attention because they can provide a high surface area for highly dispersing catalyst nanoparticles and uniform mesoporous for ion diffusion. Compared with the Vulcan carbon support, mesoporous carbon surface as catalyst supports are readily accessible for the incorporate metals due to its high surface volume ratio (Tayal et al., 2012; Wang et al., 2007; Jiang et al., 2005). Most of the research is prepared by the ordered mesoporous carbon structure of two-step micro-molding and tri block-copolymer-tinplating approaches. Further than mentioned catalyst have good application in the fuel cell technology. Now a day's fuel cell technology is very growing technology in the world. Metal catalyst is the one of the part of the enhancing performance of the fuel cell reaction. Several type of fuel cell available in the society and much kind of fuels, electrolytes and electrocatalyst are used in the chemical of the fuel cell reaction. Compared catalysts support materials most attraction fuel cell technology (Alegre et al., 2013; Alegrea et al., 2011; Moliner et al., 2008). This kind of catalyst also increases the electrochemical surface area of prepared catalyst.

In this paper represent the Pt-Ru/Vulcan, Pt-Ru/Xerogel and Pt-Ru/OMP carbon support materials for sodium borohydride methods at room temperature. The prepared catalyst are characterized by the particle size by using the transmission electron microscopy, crystallite size of prepared catalyst found that using X-ray diffracting method, morphology of the catalyst determine by scanning electron microscopy and composition of the prepared catalyst also confirmed to the energy dispersive X-ray spectroscopy. The prepared catalyst which type of metal present in the carbon support materials also confirmed the infrared spectroscopy. This prepared catalyst test about the single cell performance of the membrane less ethanol fuel cell, it's shown that better optimized activity compared the commercial available catalyst.

## Materials and methods

### Materials

The metal precursors used for the preparation of electro catalysts were  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Aldrich) and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (Alfa Aesar). Vulcan Carbon XC-72R, carbon Xerogel, and mesoporous carbon (Cabot Corp.,) was used as a support for the catalysts. Graphite plates (3 cm long and 0.1 cm wide, E-TEK) were used as substrates for the catalyst to prepare the electrodes. Deionized water (DI) (Merck) was used as the solvent;  $\text{NaBH}_4$  (Merck) was used as reduction agent. Nafion<sup>®</sup> (DE 521, DuPont, USA) dispersion was used to make the catalyst ink. Ethanol (Merck), sodium perborate (Riedel) and  $\text{H}_2\text{SO}_4$  (from Merck) were used as the fuel, the oxidant and as the electrolyte for electrochemical analysis, respectively; all the chemicals were of analytical grade. Pt/C (40 wt%, E-TEK) was used as the cathode catalyst.

### Preparation of catalyst

The Pt-Ru/Carbon support catalyst prepared by the sodium borohydride reduction method (Alegrea et al., 2011; Moliner et al., 2008; Cinthia et al., 2013). Required amount of metal precursors dissolved in deionized water. The aqueous solution is stirred at room temperature for 1 hour. The prepared solution is maintained basic nature added to the NaOH solution required amount. The small quantity of the carbon support is dispersed in the deionized water and stirrer the solution gets the homogeneous mixture. Subsequently above the solution added to the homogeneous mixture then aqueous solution of  $\text{NaBH}_4$  added carefully and

the suspension was stirred for 2h left to settle all the precipitate. Finally the precipitate was filtered and washed with deionized water dried in a vacuum oven at 80°C. Further the catalyst studied about the physical and chemical characterization.

### Characterization

The transmission electron microscope (TEM) Zeiss109 was used to observe morphological structure and determine the particle size of the prepared catalysts. Energy dispersive X-Ray spectroscopy (EDX) used to determine the composition of metal present in the prepared catalyst. XRD patterns of the catalysts were obtained on a X-ray diffractometer-Rigaku D/Max-2200V-PC using a Cu K  $\alpha$  source ( $\lambda = 1.5418 \text{ \AA}$ ) at a scan rate of 1.5°/min. the scan range was operating at room temperature. The mean particle size analyzed from TEM is verified by determining the crystallite size from XRD pattern using Scherer formula.

## Results and discussions

### X-ray diffraction (XRD)

The XRD patterns of the prepared Pt-Ru/Vulcan, Pt-Ru/XC, and Pt-Ru/OMP catalysts are shown in Fig. 1. The diffraction peaks seen in all the diffraction patterns at around 25° and 26° are associated with (002) plane carbon support. The diffractogram of Pt-Ru electrocatalyst show peaks the (111), (200), (220) and (311) crystalline planes respectively, of the face centered cubic (fcc) structure characteristic of platinum and platinum alloys. No diffraction peaks of the Ru structure are observed. It is clearly explain that Ru is incorporated into the Pt surface (Tayal et al., 2012; Alegre et al., 2013). Prepared all the catalyst shows higher 2 $\theta$  values comparing to the monometallic catalyst.

Table 1 shows lattice parameter of Pt-Ru/Vulcan (0.3912), Pt-Ru/CX (0.3889) and Pt-Ru/OMP (0.3917). This decreased lattice parameter value one of the evidence for Pt-Ru alloy formation. Lattice contraction shows that prepared all catalyst have amorphous structures. Pt crystallite sizes calculated is good agreement with the particle size calculated using Tem. The crystallite sizes of the synthesized catalyst is calculated with scherrer formula  $d = K\lambda/\beta \cos\theta$ , wherever k (=0.9) be the shape factor, d=average particle size,  $\lambda$  be the wave-length of Cu K $\alpha$  in radians. The crystallite size of the synthesized catalyst varies in the range of 3-5 nm.

Table 1. The EDX composition, lattice parameters, and the particle size obtained for different atomic ratios of electrocatalysts

S. No.	Catalysts	Atomic ratio	2 $\theta$ Value	Lattice parameter (nm)	Crystallite size (nm)	Particle size from (TEM) nm
1	Pt–Ru/Vulcan	86:14	67.64	0.3914	4.8	4.0
2	Pt–Ru/CX	55:35	68.17	0.3887	4.6	3.9
3	Pt–Ru/OMP	84:16	67.87	0.3901	4.0	3.6

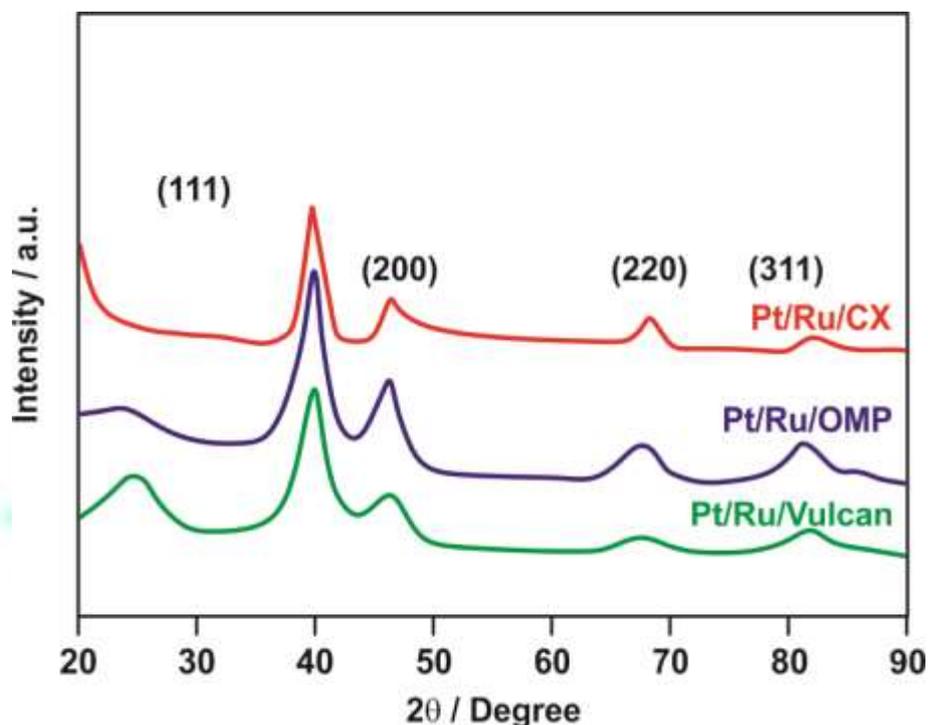


Fig. 1. X-ray diffraction patterns of Pt–Ru/OMP (80:20), Pt–Ru/CX (50:40) and Pt–Ru/Vulcan (80:20) catalysts

### Transmission electron microscopy (TEM)

The TEM images of the Pt-Ru/OMP, Pt–Ru/XC, and Pt–Ru/Vulcan catalysts are presented in Fig 2. a–c, respectively. The metal particles on Pt-Ru/Vulcan evenly distributed comparing to another carbon support and particle size is slightly higher than that of carbon supports. Pt-Ru/XC also evenly distribution of particle size and slightly higher particle size comparing to the Vulcan carbon support. Fig 2. TEM image of Pt-Ru/OMP shown agglomeration for the prepared catalyst. It is evidence of the more number of oxygenated species present in the carbon support materials. The heavy black dots on the carbon support are the catalyst particles. The obtained average particle sizes is about 3-5 nm which is reasonably good concurrence with those estimated by XRD. The table showed that Pt<sub>80</sub>–

Ru<sub>20</sub>/Vulcan slightly smaller mean particle size comparing to Pt<sub>80</sub>–Ru<sub>20</sub>/CX, and Pt<sub>80</sub>–Ru<sub>20</sub>/OMP. The particle size distribution of these catalysts is shown in Table 1 in accordance to the TEM images.

### EDAX (Energy Dispersive X-ray Spectroscopy)

The EDX spectra of Pt–Ru/OMP, Pt–Ru/CX, and Pt–Ru/Vulcan catalysts are shown in Fig. 3 Confirm the presence of Pt, Ru on the carbon support. The EDX result shows the table1. The catalysts are prepared had the desired elements with some variation in composition. The atomic ratios of Pt-Ru/OMP, Pt-Ru/CX and Pt-Ru/Vulcan catalysts are 86:14, 55:35 and 84:16. The EDX results of the catalysts are very close to the theoretical values, which designate that the metals were burdened onto the carbon support exclusive of understandable loss.

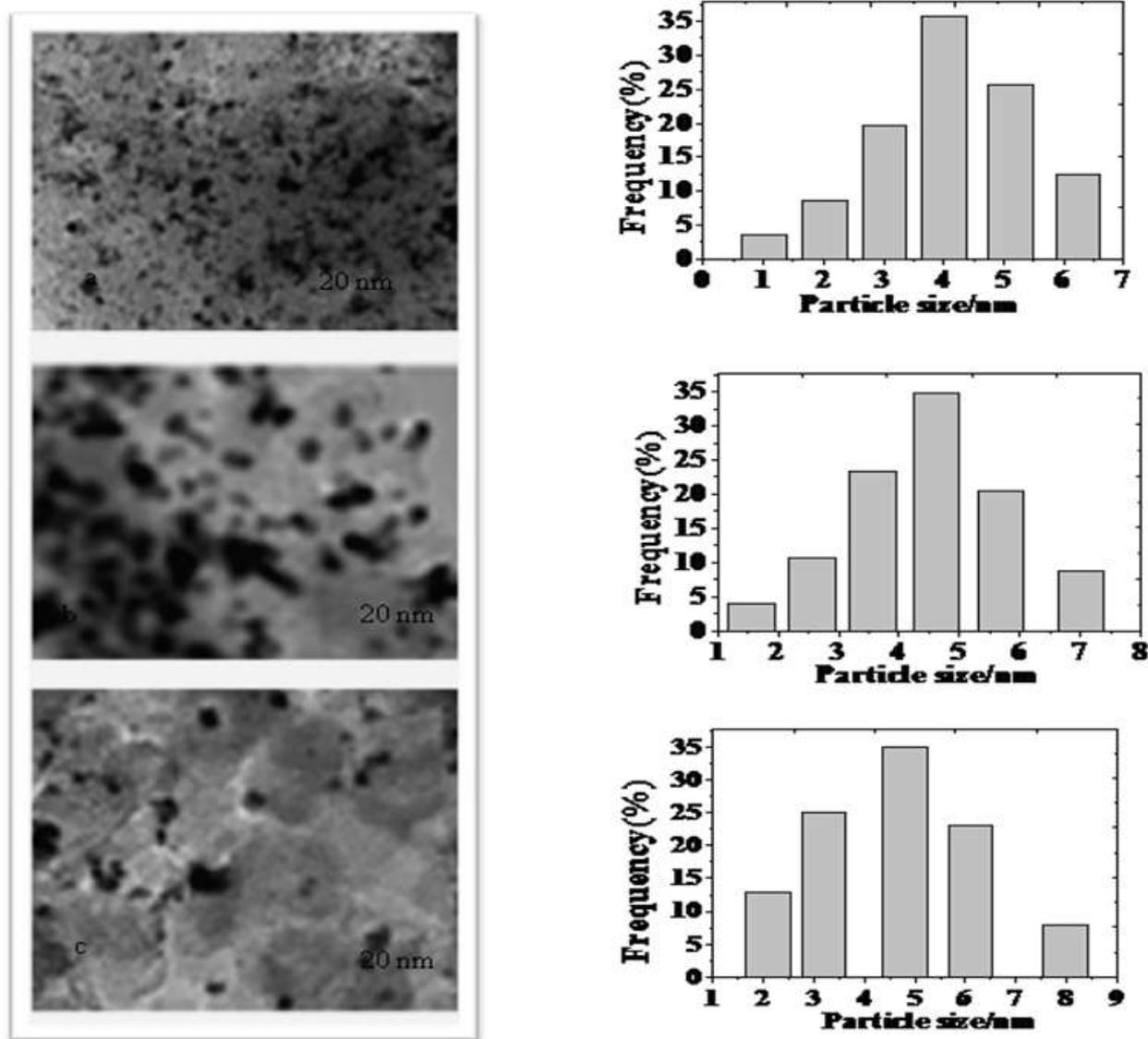


Fig. 2. TEM images of (a) Pt-Ru/OMP, (b) Pt-Ru/CX, and (c) Pt-Ru/Vulcan catalysts

#### Energy Dispersive X-ray Spectroscopy (EDAX)

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#### Electrochemical measurements

**Cyclic voltametric:** Fig. 4 Shows the cyclic voltammograms (CV) of ethanol oxidation under acidic conditions (1.0 M  $C_2H_5OH$  and 0.5 M  $H_2SO_4$ ) catalyzed by Pt-Ru/XC (50:40), Pt-Ru/OMP (80:20), Pt-Ru/C and (80:20), catalysts. All the current values were normalized

by the geometric surface area of the electrode used. Compared to the onset potential of Pt-Ru based catalyst negatively shifted those obtained the monometallic Pt-based catalyst. This is due to the Presence of Ru in the Pt surface and formation of the  $Ru-OH_{ads}$  type at lowers potentials, helping to oxidize the  $CO_{ads}$  through the bifunctional mechanism and electronic effect. There were three oxidation peaks when ethanol CV was carried out on the PtRu/carbon based catalyst (vs. Ag/AgCl), two during the forward scan and one during the reverse scan. The main results of CV test of Pt-Ru/CX (50:50), Pt-Ru/OMP (80:20), Pt-Ru/C (80:20), catalysts are listed in Table 2 including the positive peak potentials and corresponding peak current densities of ethanol electro-oxidation. Figure 4b shows that the onset potentials of ethanol electro oxidation for Pt-Ru/CX (50:50), and Pt-Ru/OMP (80:20) and Pt-Ru/C (80:20) are

at about 400 V. In addition carbon support catalysts enhance ethanol oxidation comparing to the Pt-Ru/C carbon. It may be carbon support and Pt-Ru binary catalyst shown the strong interaction during the oxidation reaction in low

potential. For the reason that all the catalyst is prepared same condition and same atomic ration. Additionally conclude that support materials increase CO oxidation in the fuel cell reaction.

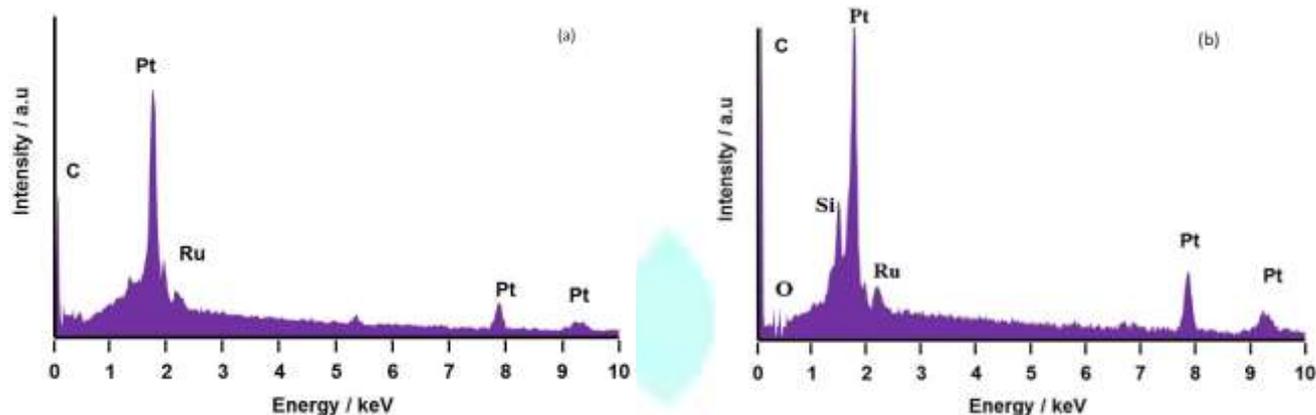


Fig. 3. EDX spectra of (a) Pt-Ru/C and (b) Pt-Ru/OMP catalysts

Table 2. CV results of, Pt–Ru/OMP (80:20), Pt–Ru/CX (50:50) and Pt–Ru/C (80:20) electrocatalysts at room temperature

S. No	Catalysts	Scan rate =50 mV	
		Positive peak potentials (mV) Ag/AgCl	Peak current density (mA /cm <sup>2</sup> )
1	Pt–Ru/CX	0.55	175
2	Pt–Ru/OMP	0.53	198
3	Pt–Ru/Vulcan	0.68	98

Pure Pt-Ru/C catalyst (Fig 4) does not behave as a very good anode for ethanol electro-oxidation due to its poisoning by strongly adsorbed intermediates such as CO<sub>ads</sub> (Viger et al., 2004). However, the introduction of carbon xerogel and ordered mesoporous carbon promotes the electrocatalytic activity. In fact, as observed in Fig4a the introduction of carbon xerogel and order mesoporous carbon leads to an increase in the electro-activity of the binary electrocatalysts. This highest current density in ethanol oxidation occur due the high electrical conductivity ordered porous structure, large surface areas and high concentration of oxygen group present in the carbon support material surface.

The presence of OH<sub>ads</sub> species in large amounts is necessary for the complete oxidation of poisoning intermediates such as CH<sub>x</sub> and CO. The carbon xerogel and order mesoporous carbon supports are performed better than vulcan carbon for ethanol oxidation. Moreover, when comparing to the Vulcan carbon another two carbon support increase the current density, low onset potential and good electrical performance.

#### Chronoamperometry test (CA)

The Pt–Ru/C, Pt–Ru/XC and Pt-Ru/OMP electrocatalyst performances for ethanol oxidation were studied by chronoamperometry (CA), to evaluate both the electrocatalytic activity of the catalysts and the poisoning of the active surface under continuous operation conditions. Fig. 5 shows representative chronoamperograms obtained for the different electrocatalysts whose current densities were normalized by Pt catalyst at 0.60 V. Through the first few minutes, the current was suddenly decreased and after some times the stable current is occur. It is due to the formation of the CH<sub>x</sub>, CH<sub>3</sub>CHO and CH<sub>3</sub>COOH poisoning of the Pt surface and the accumulation of the Ru-OH in the Pt surface.

The support materials Pt–Ru/CX (50:50), Pt–Ru/OMP (80:20) electro-catalysts gave higher current than the binary Pt–Ru/C (80:20) electro-catalyst. Higher current obtained for the electrocatalysts due do the support, since all the catalyst have same atomic surface area, similar particle size. This may indicate a change the support in structural defects or roughness,

making the support materials better candidates for ethanol electro-oxidation. These observations suggest that the optimized performance of Pt-Ru/support due to the high porosity, large electrochemical surface area, durability of the prepared electrocatalysts.

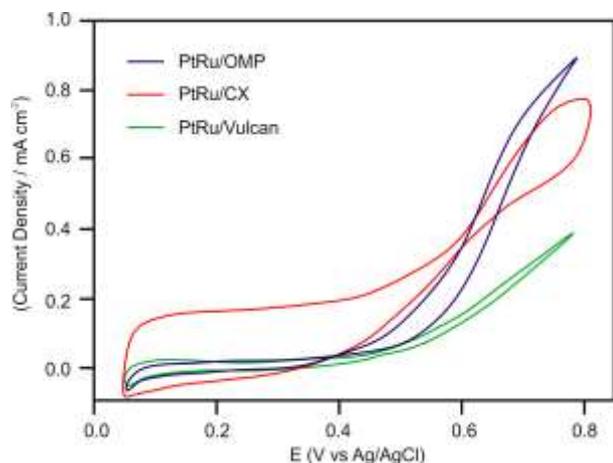


Fig. 4. Cyclic voltammetry of Pt-Ru/OMP (80:20), Pt-Ru/CX (50:50) and Pt-Ru/C (80:20) electrocatalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M ethanol at room temperature with a scan rate of 50 mV/s

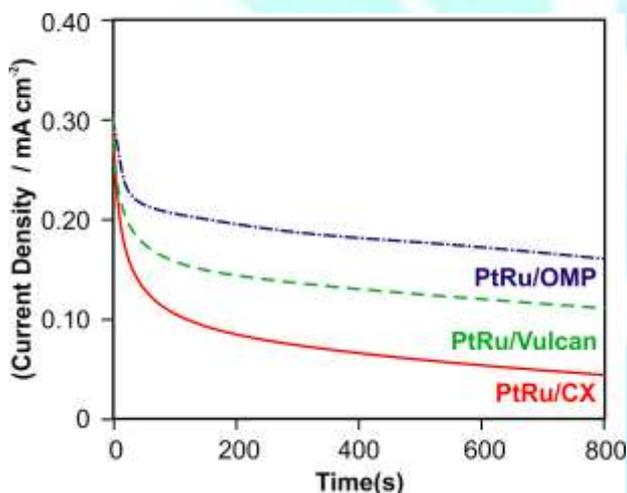


Fig 5. Chronoamperometry of Pt-Ru/OMP (80:20), Pt-Ru/CX (50:50) and Pt-Ru/C (80:20), electrocatalysts at room temperature

### Conclusions

The Pt-Ru/OMP, Pt-Ru/CX and Pt-Ru/C catalysts are prepared by borohydride reduction method at room temperature. Prepared electrocatalyst characterized by XRD, TEM, and EDX spectra. The particle size of prepared catalyst calculated using sherrer formula and particle size is confirmed to 3-5 nm it is good agreement with the XRD pattern of crystallite size. Composition of the Pt-Ru catalyst observed from the EDX it is very close to the theoretic value. It's shown that synthesized catalyst has a

high accessible surface area, pore size distribution, good electrical conductivity, and best surface chemistry. Cyclic voltammetry results showed that Pt-Ru carbon supports catalyst is best active in ethanol electro-oxidation than commercial present carbon support catalysts. Chronoamperometry results also confirmed that Pt-Ru/OMP catalysts gave good stability than the Pt-Ru/CX and Vulcan carbon support Pt-Ru catalysts at steady condition. In this present work, for the first-time various supported binary Pt-Ru/OMP, Pt-Ru/XC and Pt-Ru/C anode catalysts were effectively tested in membraneless fuel cell using 1.0 M ethanol as the fuel and 0.1 M sodium perborate as the oxidant in the presence of 0.5 M H<sub>2</sub>SO<sub>4</sub> as the electrolyte. Based on the current density, onset potential of support materials enhanced performance of anode catalyst for electro-oxidation of membraneless ethanol fuel cell (MLEFC). We are except that Pt-Ru based carbon supports best catalyst for the fuel cell reaction and also produces environmentally friendly sustainable energy.

### Acknowledgments

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### References

1. Figueiredo JL, Pereira MFR, Serp P, Kalck P, Samant PV, Fernandes JB. Development of carbon nanotube and carbon xerogel supported catalysts for electro-oxidation of methanol in fuel cells, *Carbon* 44 (2006) 2516-2522.
2. Calvillo L, Gangrei M, Perathoner S, Centi G, Moliner R, Lazaro MJ. Hollow Macroporous Core/Mesoporous Shell Carbon with a Tailored Structure as a Cathode Electrocatalyst support for proton exchange membrane fuel cell, *Journal of Power Sources* 192 (2009) 144-150.
3. Moliner R, Lazaro MJ, Calvillo L, Sebastian D, Echegoyen Y, Garcia-Bordeje E, Salgado JRC, Pastor E, Cabot PL, Esparbe I. Oxidised carbon nanofibers as platinum support for proton exchange membrane (PEM) fuel cells, *Sensor Letters* 6 (2008) 1059-1067.
4. Li X, Hsing IM, The effect of the Pt deposition method and the support on Pt dispersion on carbon nanotubes, *Electrochimica Acta* 51 (2006) 5250-5258.

5. Jiang Z, Jiang J, Meng Y. High catalytic performance of Pt nanoparticles on plasma treated carbon nanotubes for electrooxidation of ethanol in a basic solution, *Applied Surface Science* 257 (2011) 2923-2928.
6. Fang B, Kim JH, Lee C, Yu JS. Carbon xerogels as catalyst supports for PEM fuel cell cathode, *Energy Conversion and management*, *J Phys Chem* 112 (2008) 639-645.
7. Zhang C, Xu L, Shan N, Sun T, Chen J, Yan Y. Enhanced electrocatalytic activity and durability of Pt particles supported on ordered mesoporous carbon spheres, *ACS Catal* 4 (2014) 1926-1930.
8. Tayal J, Rawat B, Basu S. Effect of addition of rhenium to Pt-based anode catalysts in electro-oxidation of ethanol in direct ethanol PEM fuel cell, *International Journal of Hydrogen Energy* 37 (2012) 4597-4605.
9. Wang ZB, Yin GP, Lin YG. Synthesis and characterization of PtRuMo/C nanoparticle electrocatalyst for direct ethanol fuel cell, *Journal of Power Sources* 170 (2007) 242-250.
10. Jiang L, Sun G, Liu J, Tang S, Li H, Zhou B, Xin Q. Structural and chemical composition of supported Pt-Sn electrocatalysts for ethanol oxidation, *Electrochimica Acta* 50 (2005) 5384-5389.
11. Alegre C, Elena Galvez M, Baquedano E, Moliner R, Pastor E, Jesus Lazaro M. Oxygen- Functionalized Highly Mesoporous Carbon Xerogel based Catalysts for Direct Methanol Fuel Cell Anodes, *J Phys Chem C* 117 (2013) 13045-13058.
12. Alegrea C, Caivillo L, Moliner R, Gonzalez-Exposito JA, Guillen-Villafuerte O, Martinez Huerta MV, Paetor E, Lazaro MJ. Pt and Pt-Ru electrocatalysts supported on carbon xerogels for direct methanol fuels cells, *Journal of Power Sources* 196 (2011) 4226-4235.
13. Moliner R, Lazaro MJ, Calvillo L, Sebastian D, Echegoyen Y, Garcia-Bordeje E, Salgado JRC, Pastor E, Cabot PL, Esparbe I. Oxidised carbon nanofibers as platinum support for proton exchange membrane(PEM) fuel cells, *Sensor letter* 6 2008 1059-1067.
14. Salgado JRC, Quintana JJ, Calvillo L, Lazaro MJ, Cabot PL, Esparbe I, Pastor E, Carbon monoxide and methanol oxidation at platinum catalysts supported on ordered mesoporous carbon: the influence of functionalization of the support, *Physical Chemistry Chemical Physics* 10 (2008) 6796-6806.
15. Vigier F, Coutanceau C, Hahn F, Belgsir EM, Lamy C, On the mechanism of ethanol electro-oxidation on Pt and Pt-Sn catalysts: electrochemical and in situ IR reflectance spectroscopy studies, *J Electro analytical Chemistry* 563 (2004) 81-59.

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