



## **SYNTHESIS AND CHARACTERIZATION OF TERNARY Pt-ALLOY NANO PARTICLES FOR HYDROGEN FUEL CELL APPLICATION**

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### **ABSTRACT**

**A novel ternary PtM<sub>2</sub> nano structures was prepared using simple solvothermal process. The alloy formation has been ascertained using different characterizations techniques such as X-ray diffraction, Tunneling electron microscope TEM, Scanning electron microscope SEM, EDX. The XRD pattern reveals that, the peak position was shifted to higher 2θ angle specifying the presence of Co and Ni into the lattice to form an ordered L<sub>10</sub> phase with a reduced Pt-Pt distance. The thickness of the alloy was found to be ~4.3nm and interplaner distance of ~0.23nm which correlate with TEM analysis with an average particle size ~20nm and distribution of the catalyst on carbon support was also investigated by TEM images. SEM was used to obtain the surface morphology of the synthesized catalyst as well the amount of metallic loaded from EDX.**

**Key words; Platinum, Cobalt, Nickel on Carbon Support (PCN/C), Platinum, Cobalt and Nickel for 8 hour (PCN-8h), Commercial Platinum on Carbon Support (Pt/C), Oxidation Reduction Reaction (ORR), PEMFC, SEM, EDX, TEM, XRD.**

### **INTRODUCTION**

There are three major driving forces for the increasing interests in the development of fuel cells. One is the reality that fossil fuels are running out, the world primary energy consumption is expected to grow by more than 30% from 2013 to 2030, and several studies have indicated that the reserve for the crude oil and gas, the main fossil fuel resources for world energy supply, will near an end within the next 50 years, and we have to find alternative energy sources (Thinnes, 2012; Shafiee, 2009). Secondly is the efficiency of fuel cell. The other is the fact that the pollution from using fossil fuels has become an important issue of environmental concern to human health. Fuel cells utilizing hydrogen as fuels represent an important form of tomorrow's energy because hydrogen is an efficient fuel and is environmentally clean. Imagine that a stack of hydrogen fuel cells can create enough current to power a vehicle, a building and even an entire city, and the only byproduct is water, which makes fuel cells the most energy-efficient and environmentally-friendly technology on the horizon. The auto industry, which relies on oil-fuelled cars, is perhaps the biggest driving force behind the massive investment in fuel cell development<sup>3</sup>. This is understandable because the price of oil is extremely volatile and has been increasing in the past few years which are likely to continue upwards. Moreover, the harmful emissions of CO<sub>2</sub>, CO, SO<sub>2</sub>, NO<sub>x</sub>, and

volatile organic compounds into the atmosphere cause serious environmental damage, increase respiratory problems in humans, and produce "greenhouse gas" that contributes to global warming. With these problems, fuel cell technology is inevitably seen as a viable alternative. This is now attracting tremendous interest as reliable primary power source for its higher energy conversion efficiency, zero emission of air pollutant along its light weight and low temperature operation. However the major handicap of this technology is the high performance electrocatalyst that will overcome the slow nature of the cathodic ORR. Platinum is known to present the best catalytic activity for the oxygen reduction reaction (ORR) among all pure metals and when supported on a conductive carbon serves as state of the art electrocatalyst in low temperature fuel cell air cathodes (Gottesfeld *et al.*, 1997). However, due to kinetic limitations of the oxygen reduction reaction the cathodic over potential losses amount to 0.3–0.4V under typical polymer electrolyte fuel cell (PEMFC) operating conditions (Gottesfeld *et al.*, 1997). In addition, Pt is expensive and the world's supply is limited. Therefore, the development of more active and less expensive oxygen reduction electrocatalysts than pure Pt has been the subject of extensive research for a number of decades and has favored the use of suitable Pt-alloys.

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Among these, recent studies reported that Pt–Co alloys show enhanced catalytic activity compared to pure Pt for oxygen reduction (Santiago *et al.*, 2007; Koh *et al.*, 2007; Koh *et al.*, 2007; Ferne'ndez *et al.*, 2009; Do *et al.*, 2007; Koh *et al.*, 2007; Huang *et al.*, 2006; Antolini *et al.*, 2005; Slavcheva *et al.*, 2005; Salgado *et al.*, 2004; Salgado *et al.*, 2004; Salgado *et al.*, 2005; Hwang *et al.*, 2007; Antolini *et al.*, 2006). Generally, alloying of platinum using non-noble metals Pt-M (M = transition metals such as Co, Ni, Cu, Fe, Mn e.t.c) has solve so many shortcoming of Fuel cell technology. Moorthi *et al.*, (2017) fabricated one of the most durable Pt-alloy catalyst with 82% increase in mass activity after 30,000 potential cycle. Balamurugam *et al.*, (2014) synthesized a Pt-alloy catalyst with a shift of  $0.85^\circ$  toward  $2\theta$  value. Tokako *et al.*, (2012) prepared PtNi, PtCo and PtFe catalyst with enhanced electroreduction and they successfully formed an alloy of Pt with fcc structures. Changlin *et al.*, (2015) prepared an octahedral Pt<sub>2</sub>CuNi alloy nanoparticle which shows that about 80% of the particles were in octahedral morphology and the XRD result reveals a remarkable shift in the positive  $2\theta$  value direction with fcc structures. Dao-Jun Guo *et al.*, (2014) prepared PtNi alloy nanoflowers with 4-7 nm diameter grains, fcc structure and corresponding diffraction angle (111), (200), (220), (311), the diffraction peaks were slightly shifted to the high  $2\theta$  values in the PtNi particles. Despite all the above observation still more work is needed to improve the catalytic activity of ternary-Pt based catalyst and to further insight into the catalyst structure. In the literature few works was done on ternary-Pt based alloy nano catalyst. Herein, we present a simple salvothermal method for preparation of ternary PtM<sub>2</sub> (M<sub>2</sub> = Ni and Co) based nano particle where time of synthesis aside KI, that was considered as one of the factor contributing the nature and shape of the synthesized catalyst also play significant role. This was done by comparing the synthesized catalyst at 8 hrs. with another one at 16 hrs. that is PCN-8h and PCN-16h respectively. The TEM Images indicated that multiple faces were formed which later agglomerate with time from 8 hrs. to 16 hrs. during synthesis.

### MATERIALS AND METHODS

Platinum acetoacetate (Pt(CH<sub>3</sub>COO)<sub>2</sub>), Cobalt(II) acetate (Co(CH<sub>3</sub>COO)<sub>2</sub>), Nickel acetate (Ni(CH<sub>3</sub>COO)<sub>2</sub>) and polyvinyl(2-pyrrolidone) (PVP, MW 55 000, in terms of its repeating units), were purchased from Aldrich Chemicals. perchloric acid (HClO<sub>4</sub>) and solvents like NMP, Isopropyl Alcohol (IPA), ethanol and acetone were purchased from Wako Chemicals. Commercial Pt/C and catalysts were purchased from Tanaka Kikinzoku Kogyo, Tokyo, Japan.

### Synthesis

Synthesis of ternary Pt based nanoparticle under hydrothermal condition. 30 mg of (Pt(CH<sub>3</sub>COO)<sub>2</sub>), was added to 14.97 mg of (Co(CH<sub>3</sub>COO)<sub>2</sub>), 14.88 mg of (Ni(CH<sub>3</sub>COO)<sub>2</sub>), 160 mg of PVP and 0.166 g of KI all these were dissolved in 15 ml of DMF. The mixture was sonicated for 30 minutes to obtain a homogeneous mixture. A transparent solution was transferred into Teflon-lined stainless steel autoclave and kept at 150° C for 8 hrs. and 16 hrs. for different sample. Then carbon black was added to make 40% of the metal loaded sample. The mixture Sonicated for 30 minutes and kept under reflux condition at 160°C for 2 hours. The mixture was collected centrifuged, washed one time with acetone and three times with water, dried at 60 °C in drying oven and then grinded it into a fine powder, this followed by treating the nanoparticle catalyst in tubular furnace under Nitrogen atmosphere at 200°C for two hours to remove the capping agent.

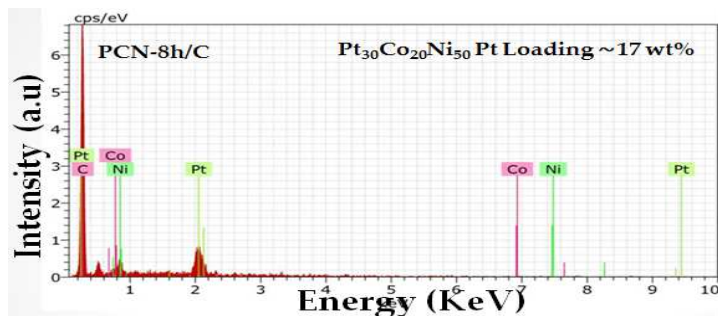
### Characterization

The resulting alloy compositions were confirmed with Scanning electron microscope SEM, energy-dispersive X-ray EDX studies to quantify the metal loading by 'Quanta 200 FEG FE-SEM'. Powder X-ray diffraction (XRD) was used to find out the structural analysis of Pt alloy nanoparticles and the measurement were performed on an X'part pro diffractometer, PAN analytical using CuK $\alpha$  line ( $\lambda = 1.5406 \text{ \AA}$ , 40 kV, 40mA) in the  $2\theta$  range of 20 to 100° with a scan rate of 2° per minute. FEI Tecnai T-20 electron microscope, operating at 200 kV was used for TEM analysis.

**RESULTS AND DISCUSSION**

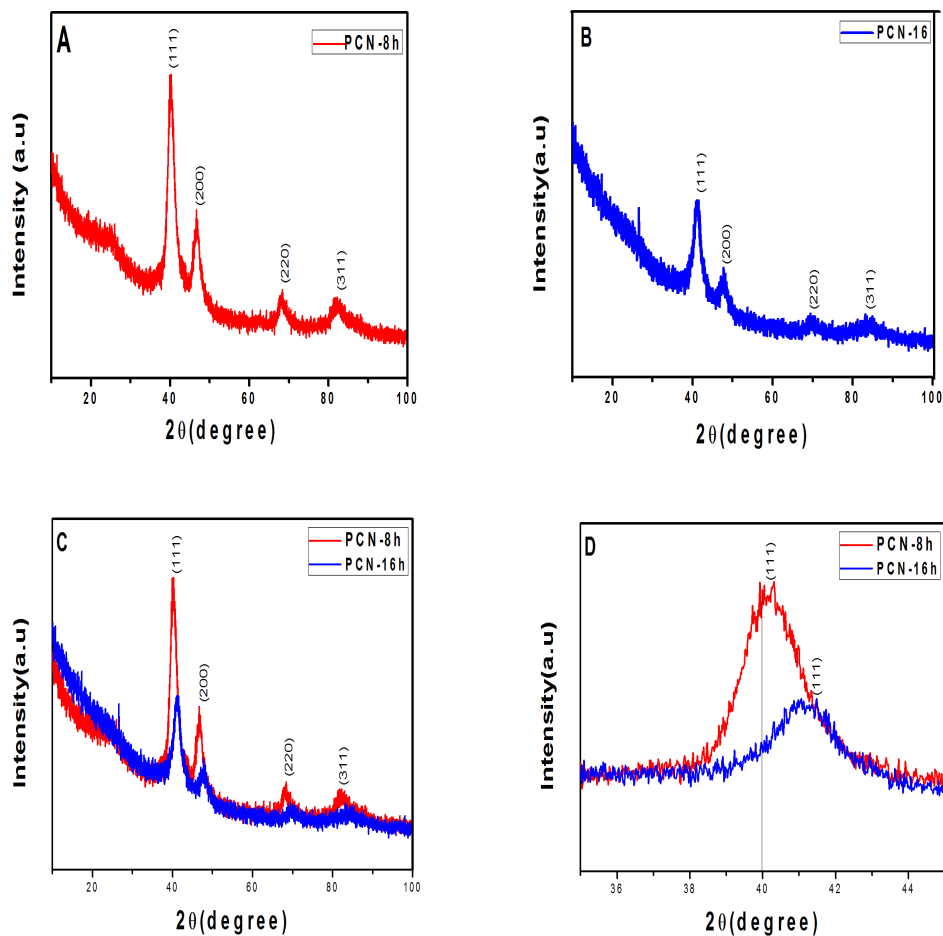
The composition of the PtNiCo/C prepared electrocatalysts was determined by EDX analysis. Fig. 1 shows the typical EDX spectrum

of the sample was found that the EDX atomic Pt:Ni:Co composition of that sample in various regions of the powders was 30:50:20, obtained for the sample prepared for 8 hrs.



Catalyst	W%Pt	W%Ni	W%Co	W%C
PCN-8h/C	16.94	8.48	3.59	70.99
PCN-16h/C	24.41	8.07	3.59	64.41

**Fig. 1.** EDX spectrum of the PCN-8h alloy catalyst obtained at 8 hours

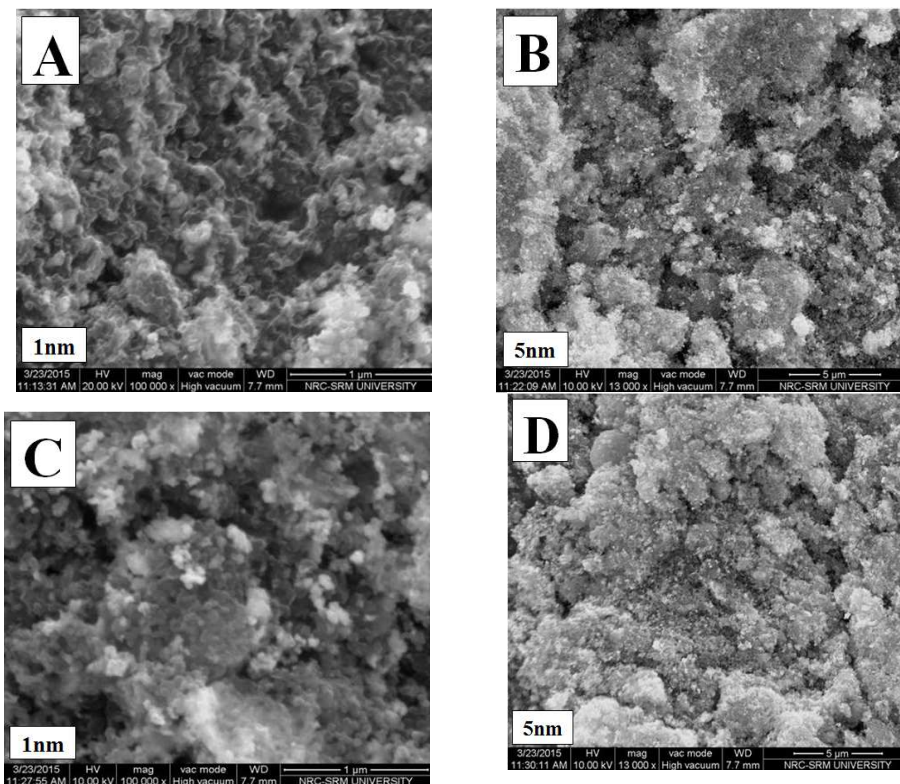


**Fig. 2** (a) and (b) XRD pattern for PCN-8h/C and PCN-16h/C catalyst, (c) is the superimposed PCN-8h/C and PCN-16h/C showing more sharper and higher peak, (d) superimposed peak (111) plane

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The presence of (111), (200), (220) and (311) plane shows the characteristic fcc structure of Pt with the introduction of Ni and Co into the fcc structure of Pt. the Pt reflex ions were shifted to higher  $2\theta$  values. fig 2c PCN-8hrs  $0.25^\circ$  shift where PCN-16hrs  $1.105^\circ$  shift. J.R.C salgado *et al* (2004). This clearly indicates the formation of an alloy. Even though there is no specific peak indicating the presence of Ni and Co. However the remarkable decrease in lattice parameters when compared to commercial Pt/C

is enough/clear indication of the incooperation of Ni and Co into the fcc of the catalyst. It was observed that the peaks were more intense in PCN8h/C more especially at (111) plane. This is attributed to the particle size. The average size of PCN-8h/C nanoparticle was estimated to be 4.3nm using Sherrer's equation. (Warren, 1969) which more precisely when compared with the broader peak for PCN-16h/C at same (111) plane (Figure 2d).



**Fig 3.** (a) and (b) low and high resolution of SEM images showing the surface morphology of PCN-8h/C. (c) and (d) low and high resolution of SEM images showing the surface morphology of PCN-16h/C

Fig. 3(a) and (b) clearly display the surface morphology of the prepared PCN-8h/C at different resolution, the appearance of the PCN/C were more clearly shown in high resolution of 5nm in which the appearance of white spot indicated alloy formation while the black colour represent the carbon support. in fig 3. (c) and (d) is the PCN-16h/C at 1nm and 5nm respectively, the image in fig. 3 (d) indicate more of the alloy on the carbon support which nearly covered all the appearance of the carbon support this give a strong agreement with the TEM images that agglomerate as the time of synthesizing the alloy increases from 8 hrs. to 16 hrs.

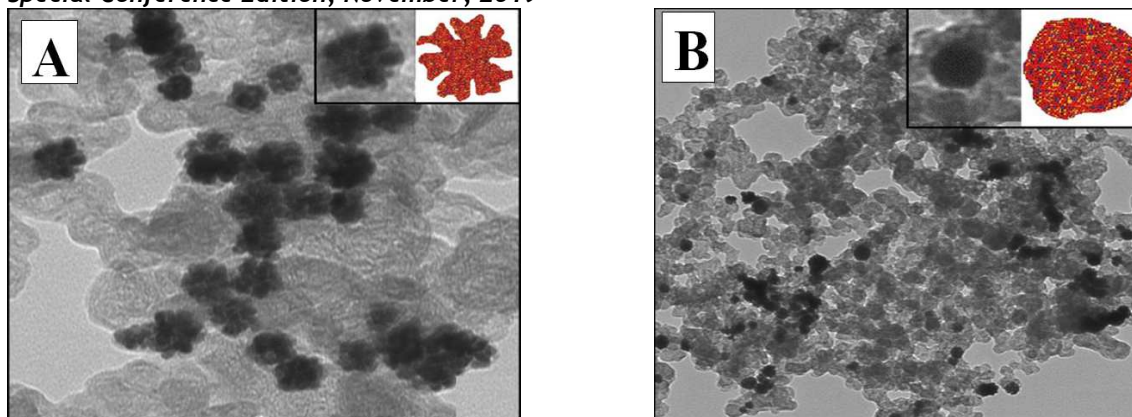
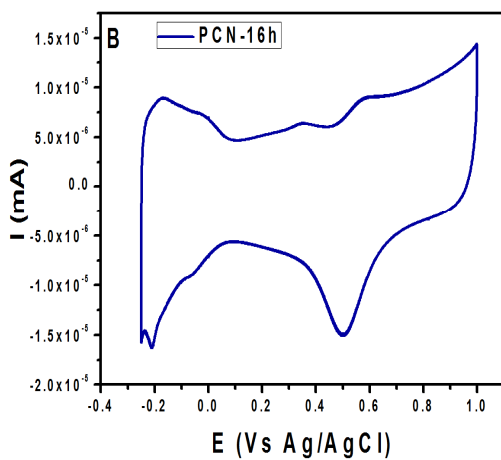
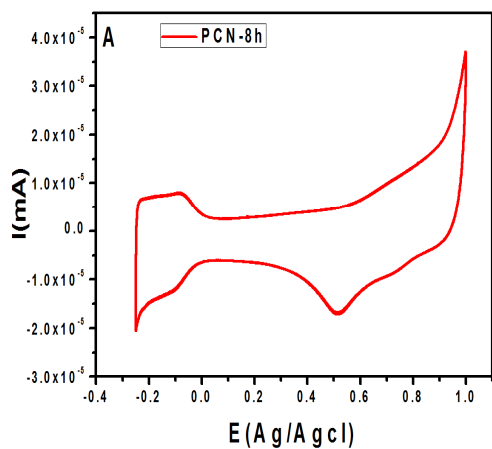
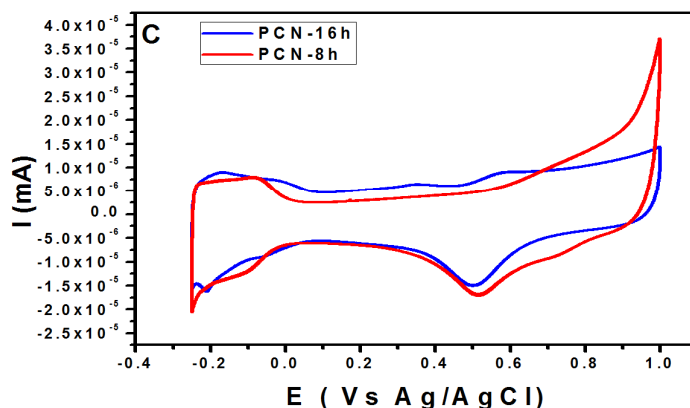


Fig.4. (a) and (b) TEM images for PCN-8h/C and PCN-16h respectively  
 Fig 4. (a) and (b) shows TEM images for PCN-8h/C and PCN-16h/C respectively but fig (a) shows multifaceted alloy which is an indication for more surface area for a reaction to take place but later the faces disappeared in fig 4 (b) this may be attributed to agglomeration. Despite the agglomeration observed for PCN-16h/C fig 4b with disappearance of many faces when compare with PCN-8h/C fig 4a still the thickness of the particles decrease from 8 to 16 hrs., likewise the interplaner distance. And both of them were having smaller interplaner distance and particle thickness compare to commercial Pt/C. See table 1.





**Fig. 5** (a) and (b) Cyclic Voltammetry curves for PCN-8h/C and PCN-16h/C respectively (c) superimposed Cyclic voltammety for PCN-8h/C and PCN-16h/C

The performance as electrocatalyst for ORR was investigated by cyclic voltammety (CV), rotating disc electrode (RDE) of 3mm diameter glassy carbon all examinations were carried out in the two electrode system Ag/AgCl as counter and reference electrodes in the presence of  $N_2$ -saturated, 0.1M perchloric acid solution at a scan rate of  $20\text{mVs}^{-1}$  to confirm the areas of hydrogen absorption, hydrogen desorption and ORR. See fig. 5 (a) and (b) for PCN-8h/C and PCN-16h/C respectively. The superimposed CV was shown in fig. 5(c) for comparison. Further investigation on electrochemical characterization will be considered in future studies.

### CONCLUSION

In summary, the multifaceted (PCN-8h/C and PCN-16h/C) alloy was successfully synthesized using simple solvothermal method. XRD result

reveals that; a shift towards high  $2\theta$  values of  $0.25^\circ$  and  $1.105^\circ$  for PCN-8h/C and PCN-16h/C respectively was observed, the particle thickness was found to be  $\sim 4.30\text{nm}$ , the interplaner distance was also found to be  $\sim 0.06\text{nm}$  less than the commercial Pt/C, the lattice parameters was  $\sim 0.01\text{nm}$  less than the commercial Pt/C. Tem analysis indicated that the particle size was  $\sim 20\text{nm}$ . In all the result it shows that, there is a strong agreement between the XRD, TEM, SEM and EDX.

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**Table 1:** Structural characteristics of the PNC-8h/C, PCN-16h/C and Pt/C electrocatalyst

Catalyst	Lattice Parameters (nm)	Interplaner Distance (nm)	Particle Thickness (nm)
Pt/C	0.3901	0.281	4.40
PCN-8hrs/C	0.381	0.22	4.26
PCN-16hrs/C	0.364	0.21	4.21

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