

## Nanocatalysts Prepared by Microwave and Impregnation Methods for Fuel Cell Application

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This work reports the preparation of Pt/C and PtCo<sub>3</sub>O<sub>4</sub>/C catalysts and shows its catalytic activity for the oxidation of methanol by using cyclic voltammetry and chronoamperometry techniques. Pt nanoparticles were dispersed by two different methods; impregnation and microwave-assisted methods over Vulcan carbon and Co<sub>3</sub>O<sub>4</sub>/Vulcan carbon. The prepared catalysts were characterized using X-ray diffraction, and transmission electron microscopy. Catalysts prepared by microwave method showed lower catalytic activity compared to impregnation method, also PtCo<sub>3</sub>O<sub>4</sub>/C composite catalysts show in general a better electro-catalytic activity for the oxidation of methanol than Pt/C. High electro-catalytic activities and good stabilities could be attributed to the synergistic effect between Pt and Co<sub>3</sub>O<sub>4</sub>. Also the dispersion of Pt nanoparticles on surface support may be improved due to the presence of Co<sub>3</sub>O<sub>4</sub>.

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**Keywords:** Fuel Cell, Nanocatalysts, Microwave synthesis, Renewable Energy, Electrocatalysis

### 1. INTRODUCTION

Fuel cell is an important technology to produce electricity through a simple electrochemical process [1]. Nanotechnology can have a direct impact on fuel cell operation and manufacturing by developing new materials with high efficiency and cost effective values [2,3]. Platinum, the main component of electrodes catalyst responsible for methanol oxidation reaction in direct methanol fuel cell (DMFC) [4,5] considered as one of the factors hinders the commercialization of fuel cell due to it

is high cost [6]. Several trials have been done to lower the cost of these electrodes by the partial replacement of the amount of platinum used [7-14]; bimetallics such as Platinum-Nickel [11,14,16], Platinum-chromium [12,16], platinum-Iron [7,11,13,16]. Also an efficient technique to reduce the amount of used platinum is by enhancing the dispersion of the platinum nanoparticles over surface of different supporting materials [5, 17]. Variation of supported material other than carbon black has shown a high effect on the catalytic activity of the prepared catalyst, such as carbon nanotube [18-20]. Also electroactivity for methanol oxidation could be increased by using metal oxides as supporting materials for Pt [21-25]. In particular, Dong et al. [26] reported that the use of 5 wt% of NiO as support for Pt catalyst showed high catalytic activity towards methanol oxidation compared to the catalyst support on Vulcan XC-72R. Same effect has been reported by Min et al [27] using NiO. In addition to that the interaction between Pt and metal oxide has been reported to increase the catalytic activity. For example Liang et al. [28] reported the using of  $\text{MoO}_x$  as support for Pt with different composition for methanol oxidation, also Justin et al. [29] studied the use of  $\text{V}_2\text{O}_5$ , which acts as promoter for Pt catalyst for enhancing its activity by twofold for methanol oxidation.

It is well known that preparation method is one of the important factors affecting the activity of electrocatalysts. One of the methods used in this work is microwave synthetic technique. Microwave synthetic technique has been used as a method for catalyst preparation due its fast, uniform, homogenous and instant heating environment, which led to fast reduction and facilitate the nucleation of metal particles [30,31]. The present study focuses on catalytic activity of Pt/C and  $\text{PtCo}_3\text{O}_4/\text{C}$  prepared by impregnation and microwave methods for the methanol oxidation. The prepared electrocatalysts are characterized using XRD, TEM and cyclic voltammetry. Stability and tolerance of prepared electrocatalysts by both of impregnation and microwave methods towards the methanol oxidation reaction have been identified using chronoamperometric measurement.

## 2. EXPERIMENTAL

### 2.1 Preparation of Pt/C and $\text{Pt/Co}_3\text{O}_4$ nanoparticles catalyst

The preparation of PtMO (M: Co) nano particles supported on carbon (Vulcan XC-72R, Cabot Corp., USA) has been done in two steps, first, an appropriate amount of M- precursors  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and carbon were mixed together with double distilled water. The MO loading was fixed at 5 wt%. The solution pH was adjusted at 10 using 1 M NaOH solution and the mixture was stirred constantly for 3 h. then the mixture was filtered, washed at least for 6 times with double distilled water and dried in an oven at 80 °C for 6 hours.

The dried mixture was then calcined at 400 °C for 3 h in air to form MO/C. Second step evolved the Pt loading onto the prepared MO/C using two methods, the impregnation method and the microwave method. The Pt loading was fixed at 25 wt%. An appropriate amount of prepared powder and Pt salt ( $\text{H}_2\text{PtCl}_6$ ) were ultrasonically mixed in double distilled water and 1 M NaOH was added in order to adjust the pH to be 11, the mixing last for 1 h at 70 °C. sodium borohydride solution was added to the mixture in which the molar ratio of Pt:  $\text{NaBH}_4$  was 1: 70, the reaction was completed

either by stirring the mixture for 3 hours in air (impregnation method) or by putting the mixture in household microwave (50 GHz, 1400 W) for 5 minutes (20 seconds on and 10 seconds off), then the resulting sample was filtered, washed at least for 6 times with double distilled water and dried in an oven at 80 °C for 6 hours.

For comparison, Pt catalyst supported on Vulcan XC-72R (Pt/C) was prepared using the two methods (impregnation and microwave) using the molar ratio of Pt: NaBH<sub>4</sub> as 1:70. According to the steps of preparation described above we prepare four samples as follow:

### 2.2 Physical characterization of the electrocatalysts

The morphology of the prepared catalysts was characterized by transmission electron microscope (TEM) (JEOL JEM 2010).

The measuring mode of the sample in TEM instrument depends on its suspension in water followed by ultrasonication for 480 s in ultra 8050-H Clifton. It was then applied in the TEM instrument on 100 mesh copper grade coated with carbon. Gatan program was used for data processing and particle size measurement.

The XRD patterns were obtained using a Rigaku-D/MAX-PC 2500 X-ray diffractometer with the Cu K<sub>α</sub> ( $k = 1.5405 \text{ \AA}$ ) radiation source operating at 40 kV and 200 mA.

### 2.3 Electrochemical measurements of the electrocatalysts

The electrocatalytic activity of Pt-metal & Pt-metal oxide supported on Carbon Vulcan XC-72R catalyst were examined towards methanol electro-oxidation in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution using cyclic voltammetry and chronoamperometry techniques for methanol oxidation using Voltalab6 potentiostat connected to a personal computer for data recording and storage. A three electrode cell was constructed in which Pt is used as the counter electrode and Hg/HgSO<sub>4</sub>/1.0 M H<sub>2</sub>SO<sub>4</sub> (MMS) as the reference electrode.

The working electrode consists of the electrocatalysts powder deposited on the surface of commercial carbon rod with active surface area of 0.5 cm<sup>2</sup>.

The surface of the electrode for each experiment was mechanically polished with emery papers in different grades.

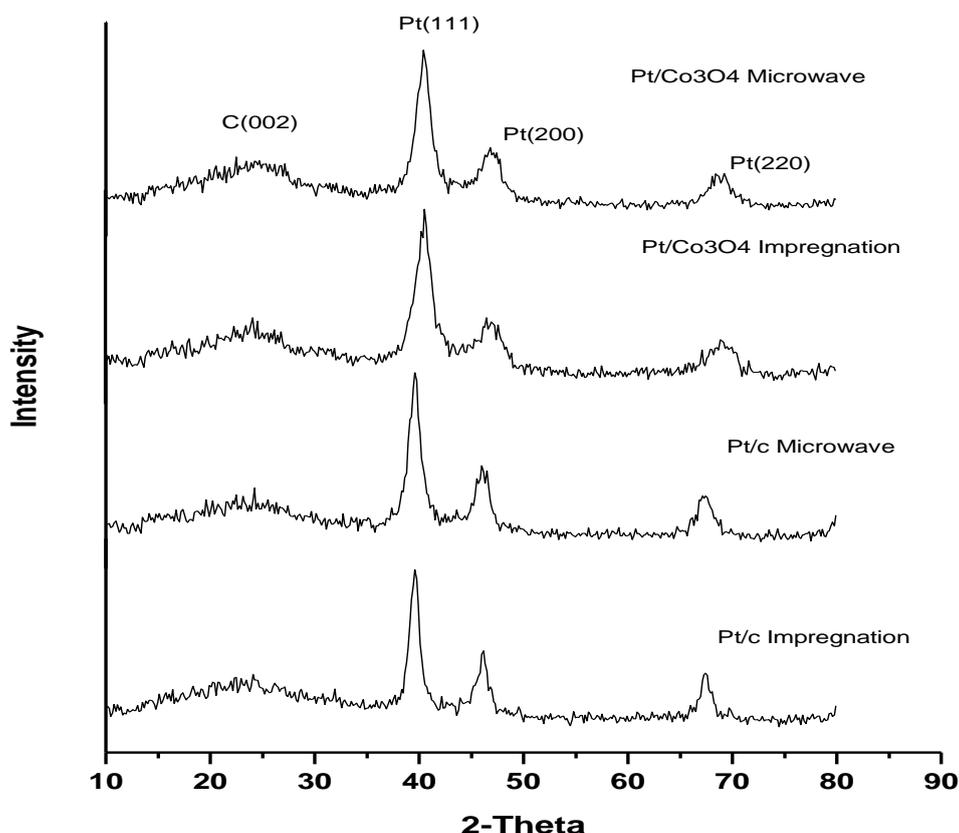
The polished surface was then rinsed with acetone followed by double distilled water. An activation step was carried out by cycling the carbon electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the potential range from -800 to +1600 mV (MMS) for 50 cycles at a scan rate of 50 mV s<sup>-1</sup>. 1.1 mg catalyst was then deposited onto the carbon surface using 5 wt.% Nafion solution (dissolved in isopropyl alcohol).

A uniform distribution of the Nafion solution was achieved by adding several doses using a microinjector. Several minutes were allowed to elapse after each dose to evaporate the isopropyl alcohol. This modified electrode was then dried at room temperature and stored in a desiccators.

### 3. RESULTS AND DISCUSSION

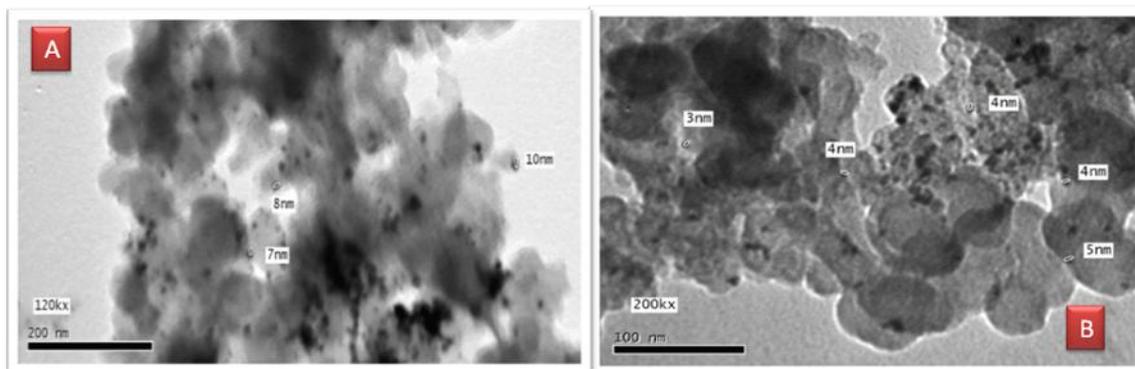
#### 3.1. Physicochemical characterization of Pt/C and PtCo<sub>3</sub>O<sub>4</sub>/C catalysts

XRD was used both to identify the phases present in our catalysts and to obtain approximate crystallite size information. Figure 1 shows a typical XRD spectra of a fresh prepared catalyst by both of impregnation and microwave methods. the wide diffraction peak at  $2\theta=24.3^\circ$  is related to the hexagonal carbon Vulcan. While, the three peaks positioned at  $2\theta=39.678^\circ$ ,  $46.173^\circ$ , and  $67.614^\circ$ (Fig.1A) and The three peaks positioned at  $2\theta=39.617^\circ$ ,  $46.044^\circ$ , and  $67.586^\circ$ (Fig.1B) correspond to the (111), (200), and (220), lattice planes of the pt/C catalyst prepared by impregnation and microwave methods in sequence. Also The three peaks positioned at  $2\theta=40.508^\circ$ ,  $46.807^\circ$ , and  $68.987^\circ$ (Fig.1C) and The three peaks positioned at  $2\theta=40.444^\circ$ ,  $46.818^\circ$ , and  $68.817^\circ$ (Fig.1D) correspond to the (111), (200), and (220), lattice planes of the PtCo<sub>3</sub>O<sub>4</sub>/C catalyst prepared by impregnation and microwave methods in sequence. The XRD spectrum of the prepared PtCo<sub>3</sub>O<sub>4</sub>/C catalysts did not show the reflections related to Co<sub>3</sub>O<sub>4</sub>. But the reflection of the PtCo<sub>3</sub>O<sub>4</sub>/C is slightly shifted to higher value compared to Pt/C patterns, which could be due to the possible interaction between the pt nanoparticles and Co<sub>3</sub>O<sub>4</sub> layers. Maiyalagan and Nawaz Khan [5] proposed that this shift could be due to the formation of an alloy between Pt and metal oxide. The synergetic effect results from that interaction may be the reason for enhancing the catalytic activity of the formed PtCo<sub>3</sub>O<sub>4</sub>/C catalyst compared to Pt/C.

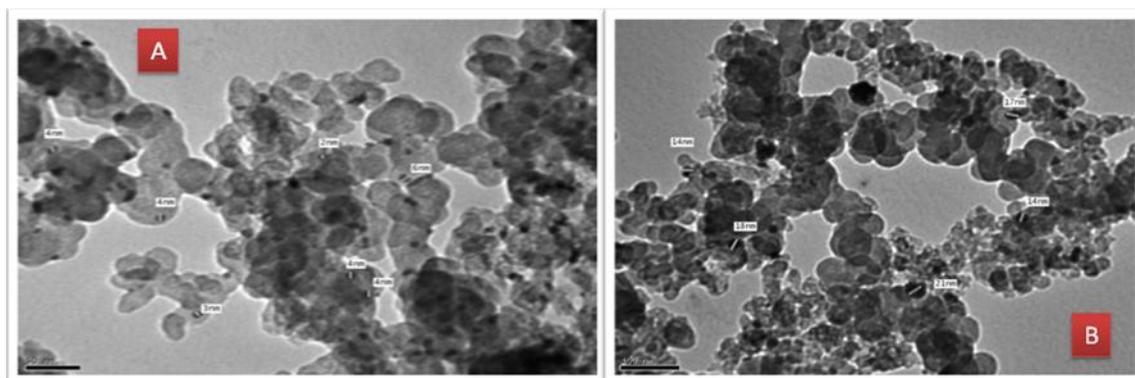


**Figure 1.** XRD patterns of Pt/C, PtCo<sub>3</sub>O<sub>4</sub>/C, catalysts prepared by impregnation and microwave methods.

The impregnation and microwave preparation methods used in this work produced a uniformly dispersion of small particles as shown in TEM images in ( Figure 2) and (Figure 3). The formation of small nanoparticles will lead to higher surface area, which reflects an increase in the catalytic activity.



**Figure 2.** TEM micrographs Pt/C obtained by Impregnation (A) and Microwave (B) synthesis methods

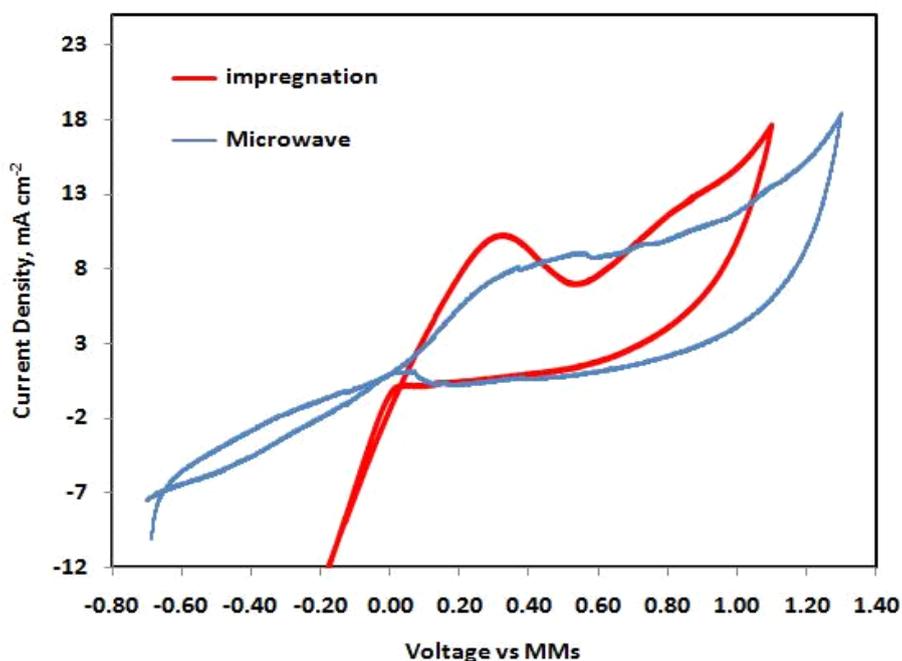


**Figure 3.** TEM micrographs Pt/CO<sub>3</sub>O<sub>4</sub> obtained by Impregnation (A) and Microwave (B) synthesis methods

### 3.2. Electrochemical characterization of Pt/C and PtCo<sub>3</sub>O<sub>4</sub>/C catalysts

Cyclic voltammetry is one of the efficient techniques that can be used to characterize and compare the electrocatalytic activity of the prepared catalysts. In this work two methods have been used to prepare the catalysts, namely the impregnation method and the microwave – assisted method. Figure 4 and 5 show the cyclic voltammograms (CVs) for methanol oxidation using Pt/C and PtCo<sub>3</sub>O<sub>4</sub>/C catalysts respectively at a scan rate of 50 mV s<sup>-1</sup>. For the Pt/C catalyst, the onset potential for methanol oxidation was about -0.05 V in both cases of using the impregnation and the microwave preparation methods. For the PtCo<sub>3</sub>O<sub>4</sub>/C catalyst, the onset potential for methanol oxidation peak was 100 mV higher than that in case of the Pt/C catalyst (+ 0.05 V) in when the impregnation and the

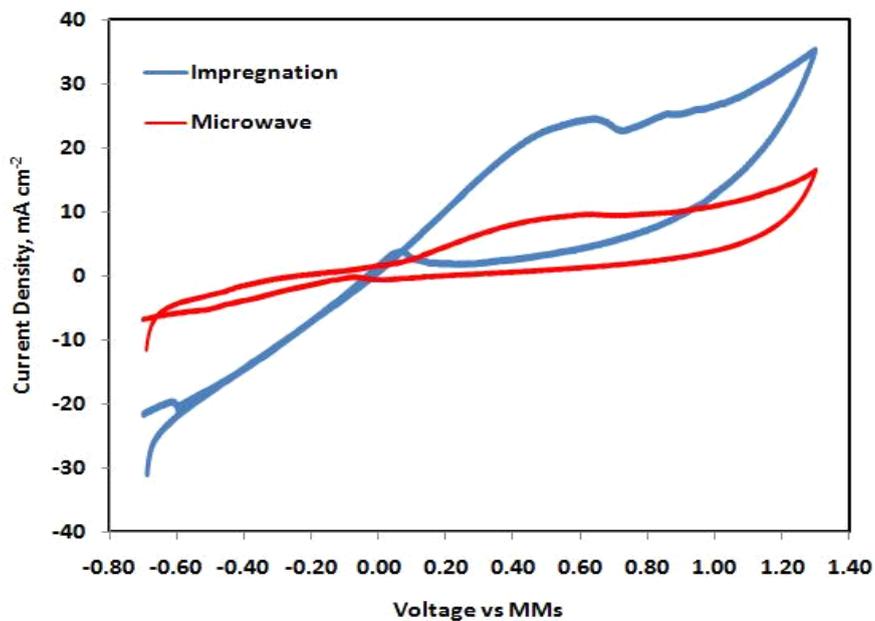
microwave preparation methods were used to prepare the catalyst. Since the potential is the thermodynamic parameter in the CVs, comparing figures 4 and 5 reveals that the PtCo<sub>3</sub>O<sub>4</sub>/C catalyst needs more activation energy compared to the Pt/C catalyst in order to undergo the oxidation of methanol on its surface. The peak current densities are about 10 and 8 mA cm<sup>-2</sup> for Pt/C and 25 and 10 for PtCo<sub>3</sub>O<sub>4</sub>/C catalysts prepared by impregnation and microwave methods respectively. Since the current is normalized to the real surface area of the active catalyst, the differences between the current densities in case of the Pt/C and the PtCo<sub>3</sub>O<sub>4</sub>/C indicate that the performance of methanol oxidation is strongly influenced by two factors; the first one is the presence of Co oxide as support material for Pt catalysts and the second one is the preparation method. Generally in case of preparing the PtCo<sub>3</sub>O<sub>4</sub> catalyst using the impregnation preparation method, the electrocatalytic activity for methanol oxidation is higher than that in case of using the microwave method as can be observed in Figure 5. In case of the Pt/C catalyst, Figure 4, the behavior is also the same. In addition, the catalysts prepared by impregnation method shows a change in the mechanism of methanol oxidation as can be deduced from the sharpness of the peak in the Pt/C catalyst prepared by the impregnation method which is shown in Figure 4.



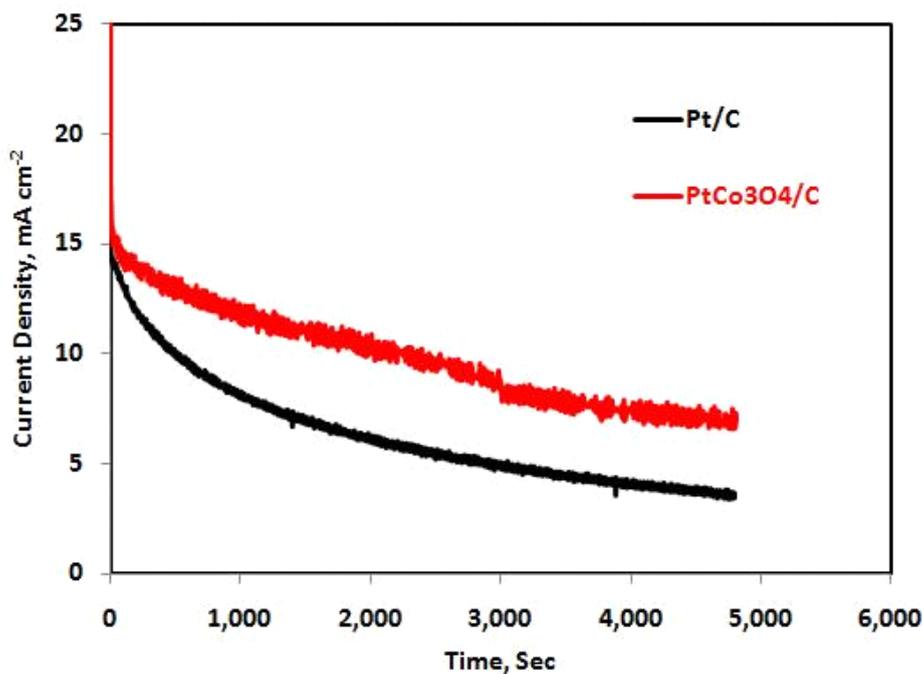
**Figure 4.** Cyclic voltammograms of Pt/C electrocatalysts prepared by impregnation and microwave method in (0.6 M MeOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>) solution The potential range is from -700 to +1300 mV at 10 mV s<sup>-1</sup>.

To measure stability and tolerance of prepared electrocatalyst by both of impregnation and microwave methods towards the methanol oxidation reaction, chronoamperometric measurement were performed in H<sub>2</sub>SO<sub>4</sub> solution containing methanol for a duration of 4800s. figures 6,7 show the current decay at fixed potential of 0.3 V of Pt/C and PtCo<sub>3</sub>O<sub>4</sub>/C electrocatalysts prepared by

impregnation and microwave methods in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.6 M Methanol. A slow decay has been observed at the polarization currents at all prepared electrocatalysts.

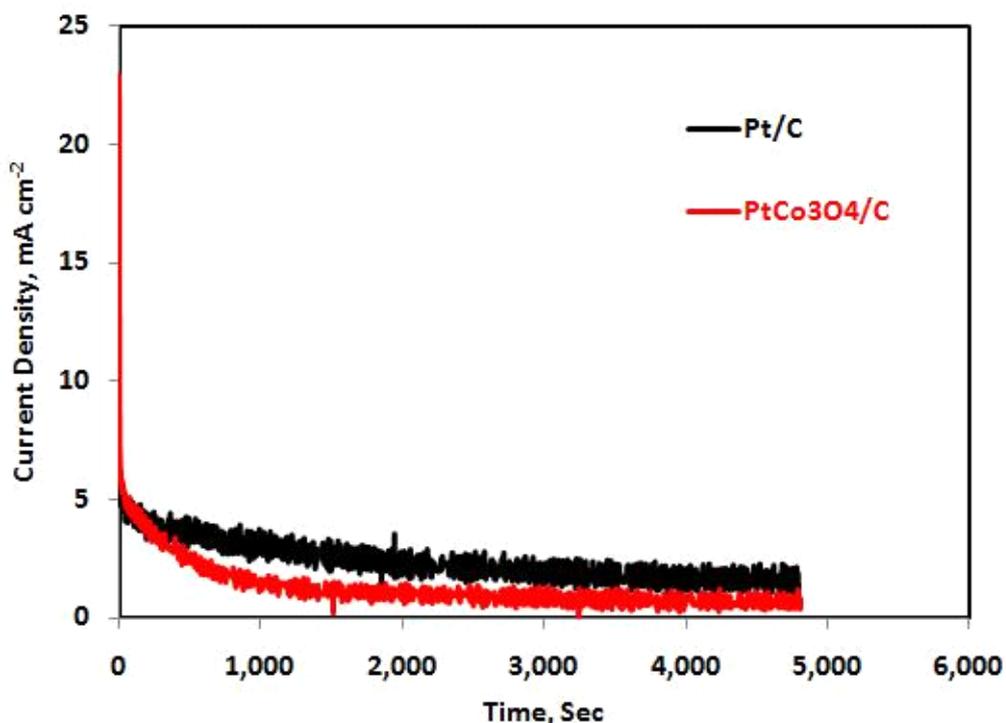


**Figure 5.** Cyclic voltammograms of PtCo<sub>3</sub>O<sub>4</sub>/C electrocatalysts prepared by impregnation and microwave method in (0.6 M MeOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>) solution. The potential range is from -700 to +1300 mV at 10 mV s<sup>-1</sup>.



**Figure 6.** Chronoamperograms of Pt/C, PtCo<sub>3</sub>O<sub>4</sub>/C electrocatalysts prepared by impregnation method at a potential value of +300 mV in (0.6 M MeOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>) solution.

The decrease in current density is due to surface poisoning induced by the intermediate CO species, such as  $\text{CO}_{\text{ads}}$ ,  $\text{CH}_3\text{OH}_{\text{ads}}$ , and  $\text{CHO}_{\text{ads}}$ , which formed during the methanol oxidation reaction.



**Figure 7.** Chronoamperograms of Pt/C, PtCo<sub>3</sub>O<sub>4</sub>/C electrocatalysts prepared by microwave method at a potential value of +300 mV in (0.6 M MeOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>) solution.

#### 4. CONCLUSION

In summary, Pt/C and PtCo<sub>3</sub>O<sub>4</sub>/C nanoparticles prepared by impregnation and microwave methods are tested for methanol electrooxidation in acidic medium. PtCo<sub>3</sub>O<sub>4</sub>/C catalyst shows higher catalytic activity towards methanol oxidation reaction compared to that of Pt/C. The presented work showed the effect of preparation method as well as the presence of Co<sub>3</sub>O<sub>4</sub> on the electrocatalytic activity of the prepared catalysts towards methanol oxidation. The results of XRD and TEM revealed that the prepared catalysts have small and uniform shapes with high dispersion ability. The developed approach is a useful method for preparing Pt and Pt supported electrocatalysts, which can be used in the field of fuel cells and other related fields.

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1. Asplund, Richard W. Profiting from clean Energy; a complete guide to trading green in solar, wind, ethanol, fuel cell, power efficiency, carbon credit industries and more, Hoboken, N.J. : John Wiley & Sons, 2008.
2. H.S. Thiam, W.R.W. Daud, S.K. Kamarudin, A.B. Mohammad, A.A.H. Kadhum, K.S. Loh, E.H. Majlan, *International journal of hydrogen energy* 36(2011)3187-3205
3. V. Baglio\*, A. Di Blasi, E. Modica, P. Creti, V. Antonucci, A. S. Aricò., *Int. J. Electrochem. Sci.*, 1(2006)71-79
4. Javier Parrondo1 R. Santhanam, Federico Mijangos, B. Rambabu, *Int. J. Electrochem. Sci.*, 5 (2010) 1342 - 1354
5. T. Maiyalagan, F. Nawaz Khan, *Catalysis Communications* 10(2009)433-436.
6. Yun Wang, Ken S. Chen, Jeffrey Mishler, Sung Chan Cho, Xavier Cordobes Adroher, *Applied Energy* 88 (2011) 981–1007.
7. Wenzhen Li, Qin Xin, Yushan Yan, *International Journal of Hydrogen Energy*, 35(2010)2530-2538
8. Antolini E., *Mater ChemPhys* ;78(2003)563.
9. Min MK, Cho JK, Cho KW, Kim H.,*Electrochim Acta* ;45(200)4211.
10. Neergat M, Shukla A, Gandhi K., *J Appl Electrochem* ;31(2001)373
11. Xiong L, Kannan A, Manthiram A., *Electrochem Commun* ;4(2002)898.
12. Pharkya P, Alfantazi A, Farhat Z., *J Fuel Cell Sci Technol*, 2(2005)171–7.
13. Li W, Zhou W, Zhou Z, Li H, Zhou Z, Zhou B, et al.,*Electrochim Acta* ;49(2004)1045.
14. Yang H, Coutanceau C, Leger JM, Alonso-Vante N, Larmy C., *J Electroanal Chem* ;205(2005)305.
15. Yano H, Kataoka M, Yamashita H, Uchida H, Watanabe M.,*Langmuir* ;23(2007)6438
16. Farid Bensebaa, Abdiaziz A. Farah, Dashan Wang, Christina Bock, Xiaomei Du, Judy Kung, and Yvon Le Page, *J. Phys. Chem. B* , 109(2005)15339-15344
17. T. Matsumoto, T. Komatsu, K. Arai, T. Yamazaki, M. Kijima, H. Shimizu, Y. Takasawa, J. Nakamura, *Chem. Commun.* 7 (2004) 840.
18. Zhao X, Li W, Jiang L, Zhou W, Xin Q, Yi B, et al., *Carbon* ;42(2004)3263
19. Li W, Wang X, Chen Z, Waje M, Yan Y., *J Phys Chem B* ;110(2006)15353
20. Chen, W.-X.; Lee, J. Y.; Liu, Z. *Mater. Lett.* , 58(2004)3166-3169.
21. C. Xu, P.K. Shen, X. Ji, R. Zeng, Y. Liu, *Electrochem. Commun.* 7 (2005) 1305.
22. M. Hepel, I. Kumarihamy, C.J. Zhong, *Electrochem. Commun.* 8 (2006) 1439.
23. C. Xu, P.K. Shen, *Chem. Commun.* 19 (2004) 2238.
24. Y. Bai, J. Wu, J. Xi, J. Wang, W. Zhu, L. Chen, X. Qiu, *Electrochem. Commun.* 7 (2005) 1087.
25. S. Jayaraman, Thomas F. Jaramillo, Sung-Hyeon Baeck, Eric W. McFarland, *J. Phys. Chem. B* 109 (2005) 2958.
26. Dong Baek Kim, Hee-Joon Chun, Yoon Kyung Lee, Heock-Hoi Kwon, Ho-In Lee, *international journal of hydrogen energy* 35(2010)313–320.
27. Min YL, Chen YC, Zhao YG, Chen C., *Mater Lett* 62(2008)4503–5.
28. Liang Ma, Xiao Zhao, Fengzhan Si, Changpeng Liu, Jianhui Liao, Liang Liang, Wei Xing, *Electrochimica Acta* 55 (2010) 9105–9112
29. P. Justin, G. Ranga Rao, *Catalysis Today* 141 (2009) 138–143
30. A.A. Elzatahry1, Hassan M. Hassan, M. ELSayed Youssef, *Int. J. Electrochem. Sci.*, 5 (2010) 1496 – 1506
31. Ching-Yi Cheng, Soundappan Thiagarajan, Shen-Ming Chen, *Int. J. Electrochem. Sci.*, 6 (2011) 1331 - 1341