

## **Platinum Nanoparticles Deposited on Oxygen-Containing Functional Groups at Carbon Vulcane XC-72 as a Cathode Catalyst for Direct Methanol Fuel Cell**

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### **ABSTRACT**

Surface oxidized carbon vulcane XC-72 is prepared as catalyst support and platinum nanoparticles are chemically anchored onto the modified surface. The nanoparticles of Pt were synthesized by reduction of H<sub>2</sub>PtCl<sub>6</sub> with sodium borohydride in a 5.5 M buffer solution of sodium citrate; the complexation of citrate with metal ions is beneficial to the formation of nanoparticles. The electro-oxidation of liquid methanol of this catalyst as a thin layer on glassy carbon electrode is investigated at room temperature by cyclic voltammetry. The results show that surface oxidized carbon vulcane support allows to obtain higher power density (about three times higher) in comparison to carbon vulcane XC-72 based electro catalyst.

**Keywords:** Carbon Vulcane XC-72; Pt Nanoparticles; Fuel Cell; Methanol Electro-oxidation; Modified glassy carbon electrode

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### **INTRODUCTION**

Among the different types of supports used in heterogeneous catalysis, carbon materials attract a growing interest due to their specific characteristics which are mainly: (I) resistance to acid/basic media, (ii) possibility to control, up to certain limits, the porosity and surface chemistry and (iii) easy recovery of precious metals by support burning resulting in a low environmental impact. Several reviews dealing with this subject have been published [1–3]. Recently, new carbon forms like graphite nanofibers (GNF) or nanofilaments and carbon nanotubes (CNT) have generated an intense effervescence in the scientific community. However, it has got to be remembered that carbon nanofilaments have been synthesized for very long as products from the action of

a catalyst over the gaseous species originating from the thermal decomposition of hydrocarbons. One of the first evidence that the monofilaments thus produced could have been nanotubes, exhibiting an inner cavity, can be found in the transmission electron microscope micrographs published by Hillert and Lange [4]. The production of graphite nanofibers is even older and the first reports date of more than a century [5, 6]. The interest in fibrous carbon has since then been recurrent and a significant boost in the research in carbon nanostructure field coincides with the discovery of multi-wall carbon nanotubes (MWNT) by Iijima [7] and the successive production of single-wall nanotubes (SWNT) [8-10].

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CNT have since then become one of the most active fields of nanoscience and nanotechnology due to their exceptional properties that make them suitable for many potential applications as polymer reinforcements for composites, or breakthrough materials for energy storage, electronics and catalysis. Of course, such a promising material attracts the interest of industrial groups that foresee a high economical impact in the near future. Currently, one of the main challenges is the low cost, industrial scale production of nanotubes that might be achieved by exploiting chemical vapor deposition (CVD) processes [11-15].

Carbon Vulcane XC-72 is one of the effective catalyst supports, which can be used widely in heterogeneous catalyst support preparation. By modification of the surface, it is supposed to have high surface activity and this subject is being concerned and investigated in this paper.

## EXPERIMENTAL

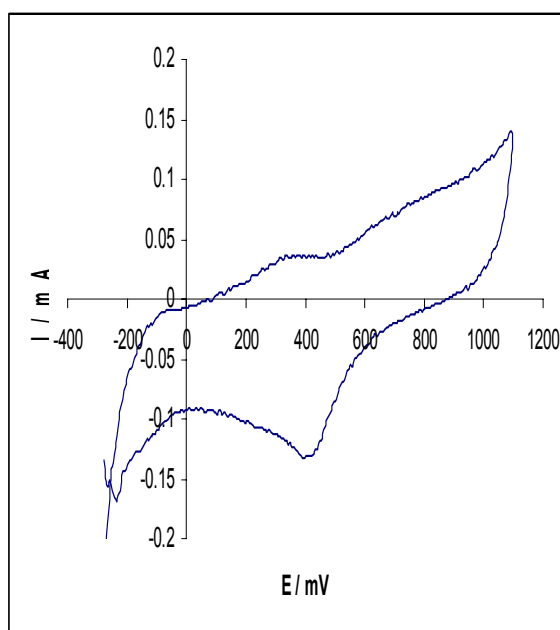
Carbon Vulcane XC-72 used in this work were purchased from Cabot Corp and were purified by ultrasonic treatment for 10 min and then refluxed in 70% HNO<sub>3</sub> at 120 °C for 4 h. Surface oxidation of the XC-72 was accomplished with a 4.0 N H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> mixture for 4 h under refluxing conditions [16].

5 mg of Carbon Vulcane XC-72 surface oxidized were added in 5 mL of 1:1 solution of distilled water and acetone then sonicated for 1h. Then 0.12 mL of 50 mM solution of H<sub>2</sub>PtCl<sub>6</sub> was added to the above mixture (20 wt. % of Pt). After, by adding sodium citrate the pH of the solution was kept in 5.5 and the mixture was stirred for 12h with a magnetic stirrer.

In a separate vessel a saturated solution of sodium borohydride (50 mg in 2 mL deionized water) was prepared and added to the above mixture drop wise and stirred for 6 h, then the mixture was centrifuged to remove the solid particles from liquid. The solid particles were heated in an oven (80 °C) for 2 h and the solid particles were collected to the experiments.

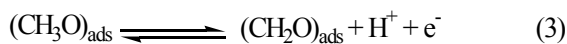
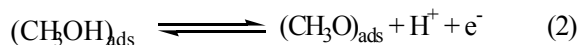
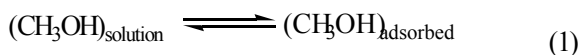
## RESULTS AND DISCUSSION

Surface modification procedures are applied to the purified Carbon Vulcane XC-72 to have the Pt particles well deposited onto it. Fig.1 Shows the cyclic voltammogram of modified glassy carbon electrode in absence of methanol, which is prepared by adding 10 μL of catalyst paste on glassy carbon electrode with Pt loading of 50 μgcm<sup>-2</sup>, 0.3 M of sulfuric acid and scan rate of 50 mVs<sup>-1</sup>. The currents show the preparation of Pt particles on XC-72 surface.



**Fig.1.** Cyclic voltammogram that shows the currents of Platinum deposited on Carbon vulcane XC-72, with 0.3 M of sulfuric acid and scan rate is 50 mVs<sup>-1</sup>.

To understand the electrooxidation mechanism of methanol in sulfuric acid solution, a typical cyclic voltammogram in presence of 0.2 M methanol is shown in Fig. 2, under the same conditions as in Fig. 1, which shows the methanol oxidation currents on Pt deposited on raw XC-72 surface (PX). According to the following sections and previous reports [18, 19] we believe, this peak involves the progress of following five steps:



Reactions from (1) to (5) can be denoted by reaction (6):

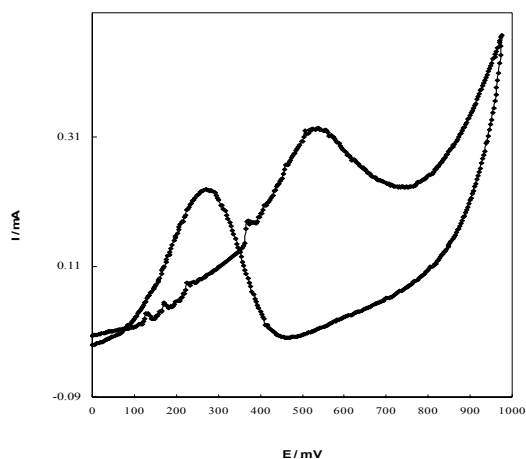


Fig.2. Cyclic voltammogram of methanol oxidation on raw carbon vulcane XC-72 (PX).

The purification and oxidation pretreatment could result in a high density of surface functional groups on the raw XC-72 surface. Among the functional groups are carboxyl, hydroxyl, and carbonyl groups which can anchor effectively the metal particles on the surface [17].

Fig3. shows the voltammogram of methanol oxidation on Pt nanoparticles deposited on surface oxidized XC-72 surface (PXO).

In Fig.4. these two catalysts (PX and PXO) are compared schematically.

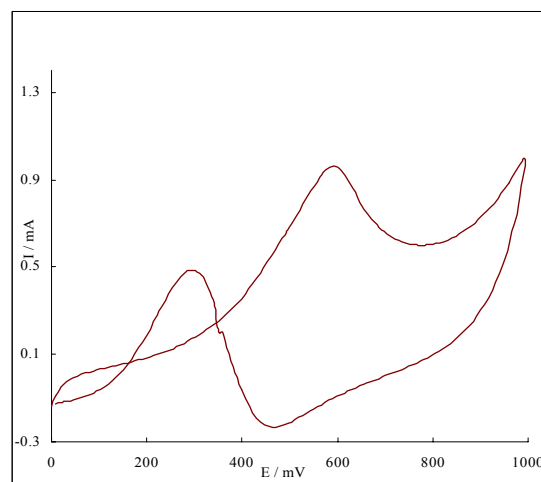


Fig.3. Cyclic voltammogram of methanol oxidation on surface Oxidized carbon vulcane XC-72 (PXO).

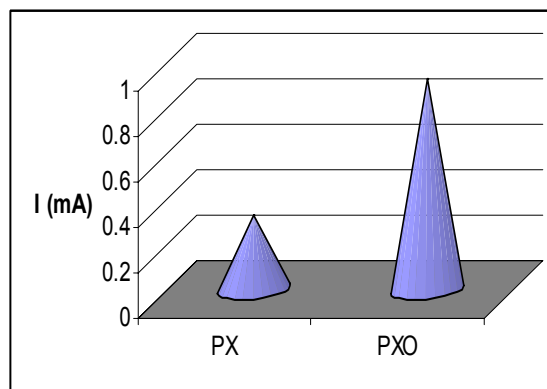
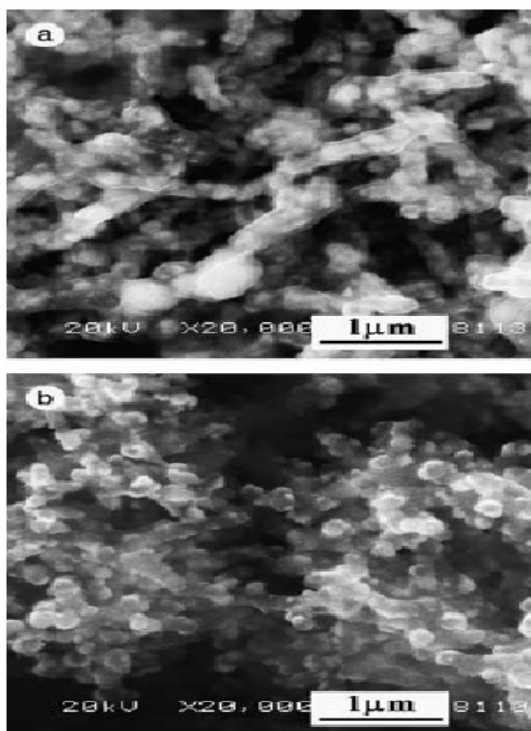


Fig.4. Schematic comparison of methanol oxidation currents on PX and PXO.

Fig.5a is the micrograph of PXO catalyst, high and homogeneous dispersion of spherical Pt metal clusters is obtained. In contrast, in the PX sample as shown in Figure 5b, Pt clusters agglomerate to some extent and disperse on the surface oxidized XC-72 no homogeneously. Pt particles have a wide particle-size distribution ranging from 2 to 5 nm. The dispersion of Pt particles may be correlated with the oxidation of XC-72 (i.e., more surface functional groups, caused by the oxidation of the XC-72 surface, appear to result in a higher density of Pt particles). The surface oxidized XC-72 is more effective in Pt deposition than XC-72 surface, maybe this factor also determines the Pt

distribution on XC-72, because Pt precursors interact with XC-72 better in oxidized form,

which results in more Pt deposition on the support.



**Fig.5.** Bright- field TEM micrograph of (a) PXO & (b)PX.

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## CONCLUSIONS

This study presents two preparation methods for Carbon Vulcane XC-72 supported platinum nanoparticle catalysts as cathode catalysts in DMFCs. Surface modification of XC-72 is found to be the key factor in controlling the particle size and distribution of Pt particles deposited on the XC-72 support.

PXO electrocatalyst shows enhanced catalytic activities and superior cell performance in comparison to PX supported Pt catalyst. The high Electrocatalytic activity may be attributed to the unique structural and higher electrical properties and the small number of organic impurities of XC-72. The Pt deposited on surface oxidized XC-72 catalyst, prepared by this method is superior to the catalyst prepared by reduction of Pt on raw XC-72, suggesting that the different morphology and dispersion of Pt in XC-72 -supported platinum catalysts also play an important role in the enhancement of methanol oxidation activity.

## ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Islamic Azad University for their support in this work.