

Pt/TiO₂-C Electrocatalysts Prepared by Chemical Vapor Deposition With High Tolerance to Alcohols in ORR

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ABSTRACT

Pt nanoparticles were synthesized by chemical vapor deposition and were deposited on carbon and TiO₂-C substrates. The Pt/C and Pt/TiO₂-C catalysts synthesized were characterized by TEM and XRD techniques. Cyclic voltammetry and rotating disk electrode measurements for the Oxygen Reduction Reaction (ORR) were investigated in acid medium in presence of alcohols as methanol and ethanol. A Pt/C commercial sample was tested at the same conditions for comparison purposes. It was found that catalyst nanoparticles were homogeneously distributed over the carbon and TiO₂-carbon substrates with a mean particle size about 3 nm. Significant differences in the electrochemical results and alcohol tolerance are observed in the samples prepared in comparison with Pt/C commercial catalyst. The methanol tolerance of the catalysts synthesized was higher compared to the ethanol tolerance. The electrochemical activity of Pt/TiO₂-C catalyst prepared with TiO₂ rutile phase was not affected by the presence of alcohols in comparison with Pt/C samples. It is explained by the thermal treatment over Pt/TiO₂-C during the synthesis process that produces a synergetic effect caused by the formation of the interface between the platinum and oxide materials where titanium oxide acts as a protecting agent of platinum nanoparticles.

Keywords: Pt nanoparticles, chemical vapor deposition, DMFC





1. Introduction

The demand for energy is increasing in our modern society. The dependence on oil-based fuels for transportation is the major cause of air pollution in the growing urban areas of the world. It has generated a great concern to find alternative sources of efficiently generated clean energy [1-2]. Direct methanol fuel cells (DMFCs) are especially attractive for this necessity. It has been considered as one of the most promising energy technologies as an alternative conventional power generating devices. These has several advantages such as high efficiency energy conversion, low emitting pollution, fuel availability as well as the reduction of the cost associated with the production, distribution and storage problems of hydrogen [3]. However, one of the most important impediments in the development of DMFC is the cross-over of alcohol through the proton conduction polymer membrane from the anode to the cathode that reduced the cell performance associated with the competition between the two reactions Oxygen Reduction Reaction (ORR) and Methanol Oxidation Reaction (MOR). The oxidation of methanol involves the formation of intermediate products, mainly CO, which are strongly adsorbed on the surface of platinum blocking consequently the active catalytic sites and thus loss of catalyst activity to the ORR [4-7]. For this reason is necessary to develop new cathode catalysts for DMFC with high catalytic activity and selectivity to the ORR that means with tolerance to the alcohol (methanol, ethanol, propanol, etc.) [8-10].

Nowadays, the best material for the ORR is the platinum nanoparticles; however as was mentioned above its excellent catalytic properties are affected by methanol presence. According to several investigations Pt-Ru alloys exhibit an effective electrochemical activity as anodes for DMFC due to the presence of Ru facilitates the oxidation of CO species, that means Ru nanoparticles confers tolerance to CO poisoning [11-12]. Other recent developments confirm that the addition of metal-oxides (RuO_x [13-14], TiO_2 [1, 13-15-19] and SnO_2 [2, 15, 22-24]) to the conventional Pt/C to produce Pt/ MO_x -C composites exhibit excellent properties as cathode fuel cells due to a change of the structural and electronic properties of platinum. Specifically, the TiO_2 -C substrate provides high resistance to electrochemical corrosion of carbon [16, 25-27]. Nevertheless, the amount of titanium dioxide and the crystalline phase (TiO_2 anatase/rutile phase) also modifies the strength of the interaction between the substrate and the metal nanoparticles [17, 21]. The positive effect of addition TiO_2 is explained by two effects: (1) changes in the Pt-d electronic properties and (2) a geometric effect that produce the contraction of Pt-Pt bonding distance leading to a favorable condition for the electrochemical reactions [12, 28]. This effect can be controlled by the physicochemical route of synthesis used. The composites are being developed by different routes of synthesis and are considered promising candidates to be used as catalyst for DMFC. Of the different methods reported for the synthesis of Pt nanoparticles, the chemical vapor deposition (CVD) technique produced in a short time (minutes) Pt supported well-dispersed nanoparticles in a range from 1 to 20 nm, depending on the chemical precursors and deposition conditions, which have been defined for different substrates [29]. Based in our previous reports where Pt/ TiO_2 -C prepared by photo-deposition [2, 16, 17] and chemical vapor deposition [27] methods exhibit an enhancement in the electrochemical stability and activity in the ORR in acid medium. In this paper we explored the electrochemical activity of Pt/C and Pt/ TiO_2 -C catalysts synthesized by CVD to carry out the ORR in presence of methanol as well as ethanol. All results were compared with a commercial sample (10 wt.%Pt/C-Etek) tested at the same conditions. The results shows significant favorable differences between catalysts prepared in comparison with commercial catalysts.



2. Experimental

2.1 Catalysts preparation by CVD

The synthesis of 10 wt.%Pt / 5wt.%TiO₂-C catalysts was carried out using a thermal horizontal tube quartz reactor by chemical vapor deposition method (CVD). On the preparation, the platinum acetyl acetonate precursor [(CH₃-COCHCO-CH₃)₂Pt], the titanium oxide rutile nanoparticles (TiO₂) and carbon (Vulcan XC-72) were mechanically mixed at room temperature on 10:5:85 weight ratio before impregnation. The mixed powders were heated at 473 K for vapor impregnation during 10 min using a total pressure of 4.5 torr, these conditions evaporated the platinum precursor. Then, the Pt precursor impregnated was moved to a higher temperature zone heated at 523 K in N₂ atmosphere (100 mL min⁻¹) for 10 min inside the tube reactor to achieve the precursor decomposition and to obtain the Pt nanoparticles onto the TiO₂-C nanocomposite [29-30].

The sample 10 wt.%Pt/C was synthesized using the same conditions above mentioned, the load of Pt:C was a 10:90 ratio.

2.2 Physical characterization techniques

X-ray diffraction (XRD) patterns of platinum base electrocatalysts prepared were collected on a Bruker D8 AXS equipment using a Cu anode (K_α, λ=1.5406 Å) and a Bragg-Brentano configuration. The angle 2θ was varied from 30 to 90° with 0.2° min⁻¹ and 35 kV. The particle size distribution and the surface morphology of platinum electrocatalysts were obtained with a Transmission Electron Microscopy (TEM) using a JEOL-JEM-2200 field emission operated at 200 kV. The dried samples prepared by CVD (Pt/C and Pt/TiO₂-C) were prepared by dispersion on ethanol by ultrasound and the resulting suspension was deposited onto a cooper mesh and dried at ambient condition before TEM analysis.

2.3 Electrochemical measurements

The electrochemical measurements were performed at 25°C, using a potentiostat in a three-electrode cell. A platinum mesh was used as the counter electrode, and a standard saturated calomel electrode (SCE=0.24 V) as the reference electrode. The potentials in this paper were related to the normal hydrogen electrode (NHE). Glassy carbon disk with a cross-sectional area of 0.19 cm² was used as a support for the thin films and used as an ink-type working electrode. The catalytic ink was prepared with 1mg of catalyst, 25 µL of 5 wt% solution Nafion® (Du Pont, 1100 EW) and 125 µL of ultra-pure water. For RDE experiments, 15 µL of this sonicated mixture were deposited on glassy carbon electrode (0.1 mg_{cat}).

Cyclic voltammetry (CV) in a nitrogen atmosphere was performed to clean the electrode surface from 0.05 to 1.2 V/NHE at 50 mV s⁻¹. 20 cycles were necessary to stabilize the system. Hydrodynamic experiments were recorded at oxygen atmosphere using an electrode disk rotating in the rotation range of 200, 400, 900, 1600 and 2500 rpm at 5 mV s⁻¹ from 1.0 to 0.2 V/NHE. The alcohol tolerance to the ORR at different rotating speed was evaluated at RT in acid medium employing two solutions as electrolyte: a) H₂SO₄ and b) alcohol + H₂SO₄ (0.5 M). Methanol Oxidation Reaction (MOR) and Ethanol Oxidation Reaction (EOR) activity was also measured by potential cyclic between 0.05 and 1.2 V/NHE in the same electrolytes.



3. Results and discussion

3.1 TEM and XRD results

Fig. 1 shows TEM images of (a) Pt/C and (b) Pt/TiO₂-C electrocatalysts prepared by chemical vapor deposition method. According to the micrographs both materials had a similar morphology with uniform distribution onto both substrates (TiO₂-C and Carbon). The mean particle size is between 2 and 4 nm with spherical or globular morphology.

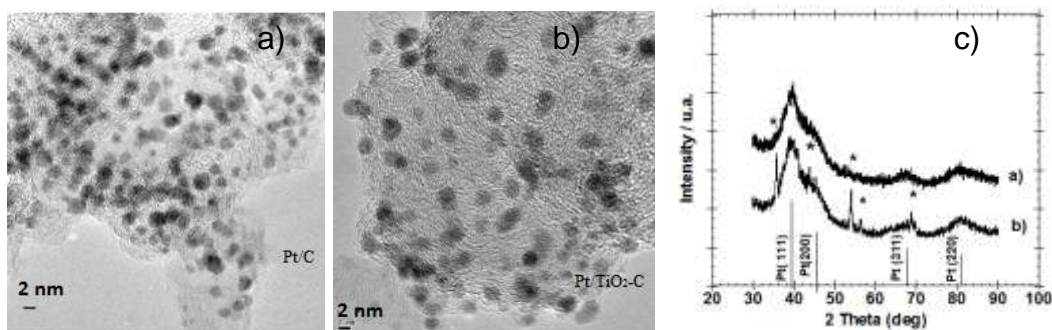


Fig. 1. TEM images of a)Pt/C and b)Pt/TiO₂-C samples synthesized by chemical vapor deposition. c)X-ray diffraction patterns of (a) Pt/C and (b) Pt/TiO₂-C electrocatalyst synthesized by CVD method. (*) refers to reflections from the TiO₂ rutile phase.

Fig. 1 (c) exhibits the X-ray diffraction patterns of Pt/C and Pt/TiO₂-C. Both materials present the crystalline face-centered cubic (*fcc*) structure of platinum. The diffraction peaks of Pt were found at 2θ values of 39.8°, 46.2°, 67.4° and 81.2° ascribed to the (111), (200), (220) and (311). For Pt/TiO₂-C electrocatalysts the presence of some reflections at 2θ values of 36.1°, 41.2°, 44.0°, 54.3°, 56.6°, 69° (indicated by asterisks) can be ascribed to the (101), (111) (210), (211), (220), (301) planes of TiO₂ rutile phase [27].

3.2 Cyclic voltammetry results

CV curves measurements were recorded in the range of potential from 0.05 to 1.2 V/NHE. The results of Pt/C and Pt/TiO₂-C catalysts synthesized by CVD are presented in Fig. 2. The CV curve of commercial Pt/C Etek is also shown in the inset of Fig 2 for comparison purposes. All shapes of the voltammograms are very similar and correspond to the typical voltammograms of Pt nanoparticles in acid medium [31-32]. Briefly, Pt samples prepared by CVD exhibit the H-adsorption/desorption peaks at 0.05-0.3 V/NHE and Pt oxide formation/reduction peaks at 0.85/0.75 V/NHE. It can be clearly seen that the Pt oxidation/reduction peaks of Pt/TiO₂-C electrode were considerably enlarged compared to the Pt/C catalysts synthesized. The



electrochemical surface area (ESA) of three catalysts was estimated by integrating the voltammograms corresponding to hydrogen adsorption-desorption area. For calculation of ESA a value of $210 \mu\text{C cm}^{-2}$ was assumed as the monolayer charge [33-34]. In this study the ESA for Pt/TiO₂-C ($5.8 \text{ m}^2 \text{ g}^{-1}$) was larger than the Pt/C ($1.1 \text{ m}^2 \text{ g}^{-1}$) indicating that more active sites are available at the Pt/TiO₂-C surfaces. According to literature the ESA for Pt increase with the Ti-oxide presence may be due to decreasing particle and because the TiO₂ presence modified favorably the structural and electronic features of platinum to carried out the H-adsorption [2, 13].

3.3 Cyclic voltammetry in presence of alcohol

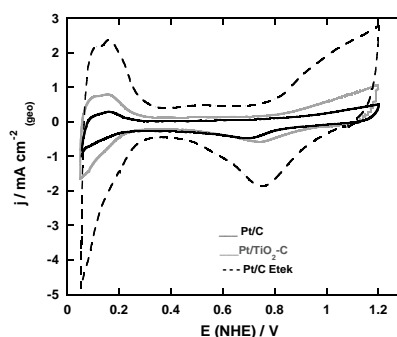


Fig. 2. CV of 10 wt.% Pt/C and 10 wt.% Pt/ 5 wt.% TiO₂-C electrocatalysts prepared by CVD compared to the commercial 10 wt.% Pt/C Etek sample in 0.5 M H₂SO₄ at a scan rate of 50 mV s^{-1} at RT.

Fig. 3 displays the CV curves obtained in presence of methanol and ethanol for Pt/C, Pt/TiO₂-C and Pt/C Etek. Also the CV curves normalized to the geometric (Fig. 3 (a-b)) and ESA values (Fig. 3 (c-d)) are presented in Fig. 3. Significant differences are observed in the Pt materials prepared compared to the commercial sample. For example in Fig. 3-a is interesting note that CV of Pt/TiO₂-C in presence of 0.5 M methanol remains almost silent, in contrast to the Pt/C and Pt/C-Etek responses. That is Pt/TiO₂-C not exhibit peaks corresponding to the oxidation and electro-oxidation methanol. This results is confirmed when CV curves are normalized to the ESA values the same observation (Fig. 3-c). Therefore Pt/TiO₂-C exhibit a remarkable methanol tolerance at a methanol concentration of 0.5 M in the same potential interval explored that Pt/C catalysts, it could be explained due to TiO₂ rutile acting as a cover protecting of platinum towards the adsorption of the methanol [21, 35]. This effect is not observed in the CV curves of ethanol presence (Fig. 3-b). That means the samples prepared by CVD including the Pt/TiO₂-C exhibit the typical characteristics of oxidation and electro-oxidation peaks of alcohol. Three samples exhibit smaller tolerance to ethanol compared to methanol presence. Is interesting observed that when CV curves are normalized to the ESA values, Pt/C catalysts exhibit the higher electro-catalytic current than Pt/TiO₂-C and Pt/C Etek materials over the whole scanning voltage range. Also the onset potential of alcohol



oxidation of Pt/C is lower than on Pt/C Etek and Pt/TiO₂-C samples. For example, Fig. 3-d shows that Pt/C electrocatalysts had a peak current of ethanol oxidation of 0.39 mA cm⁻²_{Pt} which is much higher than on Pt/C Etek sample 0.085 mA cm⁻²_{Pt} and Pt/TiO₂-C catalysts 0.08 mA cm⁻²_{Pt}. This could be caused also by the thermal (T= 473K) and pressure (P=4.5 torr) treatment during the synthesis method that change the structure and interaction of carbon with platinum.

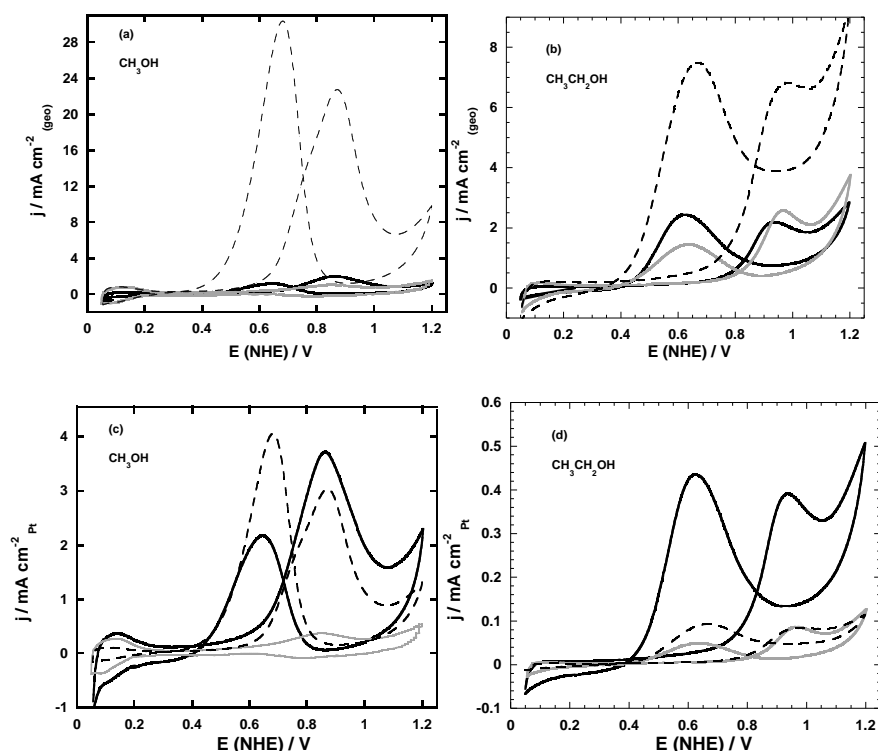


Fig. 3. Geometric (a and b) and ESA (c and d) normalized cyclic voltammograms curves of (—) 10 % Pt/C, (---) 10 %Pt/5% TiO₂-C and (- -) 10%Pt/C Etek catalysts in two electrolytes 0.5 M H₂SO₄ + alcohol (I) CH₃OH and (II) CH₃CH₂OH). Scan rate of 50 mV s⁻¹ at RT.

3.4 Rotating disk electrode studies in presence of alcohol

A rotating disk electrode (RDE) study of Pt/C, Pt/TiO₂-C and Pt/C Etek electrocatalysts to carried out the ORR in presence and absence of methanol (right) and ethanol (left) are presented in Fig. 4. The typical curves on Pt nanoparticles en acid medium exhibit the three distinct regions characteristic: (I) the kinetic region, where the current, i_k , is independent of the rotation velocity; (II) the mixed control region, where the behavior is determined by kinetic as well as diffusion processes; and (III) the mass-transfer region, where the diffusion current, i_d , is a function of the rotation velocity [37-38].



One of the most important results in this study is that the polarization curves of Pt/TiO₂-C sample are practically unchanged by the presence of 0.5 M methanol solution.

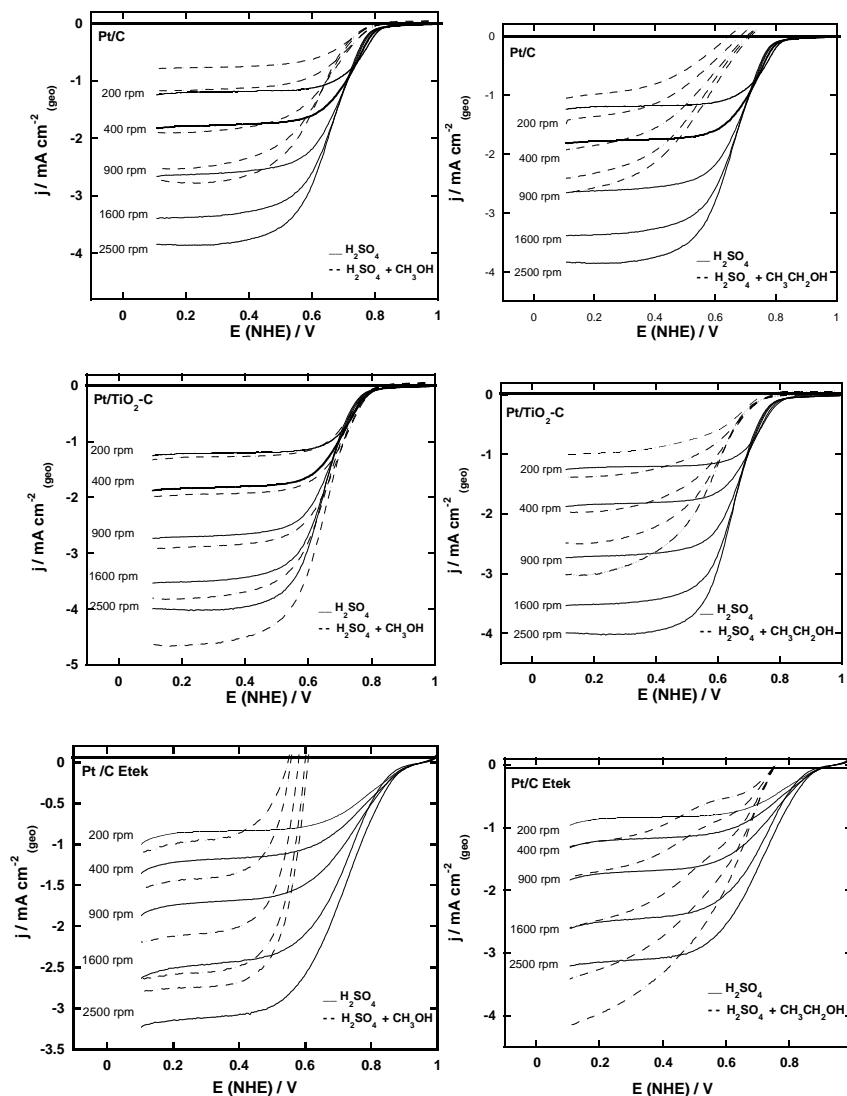


Fig. 4. Oxygen reduction reaction (ORR) curves of 10% Pt/C and 10% Pt/5% TiO₂-C prepared by CVD compared to 10% Pt/C Etek in two electrolytes 0.5 M (I) H₂SO₄ + CH₃OH and (II) H₂SO₄ + CH₃CH₂OH at different rotating speed. Scan rate of 5 mV s⁻¹ at RT.

These features are in agreement with the corresponding cyclic voltammograms of Pt/TiO₂-C in presence of methanol in Fig. 3-c. As is expected Pt commercial catalyst shows a mixed potential due to the



simultaneous methanol oxidation and oxygen reaction on its surfaces. In the case of Pt/C catalysts prepared by CVD its polarization curves also showed methanol tolerance, the net cathodic current onset of Pt/C is shifted negatively by 0.15 V/NHE, however this value is lower compared to the over-potential obtained for Pt/C Etek (0.4 V/NHE).

Right of Fig. 4 displays the polarization curves of three samples in presence and absence of ethanol. Important changes are observed compare to the results obtained in methanol. Pt/TiO₂-C sample exhibit the smaller cathodic current shifted of 0.10 V/NHE respect to the results obtained in absence of ethanol. In the case of Pt/C and Pt/C Etek, simultaneous methanol oxidation and oxygen reduction was observed. These results indicated that samples synthesized by CVD (Pt/C and Pt/TiO₂-C) had more tolerance to carried out the ORR in presence of methanol compared to ethanol

The electrochemical activity for ORR and its stability are favorable modified by the TiO₂-carbon substrate and the interaction between Pt. With these results we conclude that the synthesis method produce changes in the Pt electronic and geometric parameters intensely labeled by the presence of TiO₂ for to be used in fuel cells of alcohols.

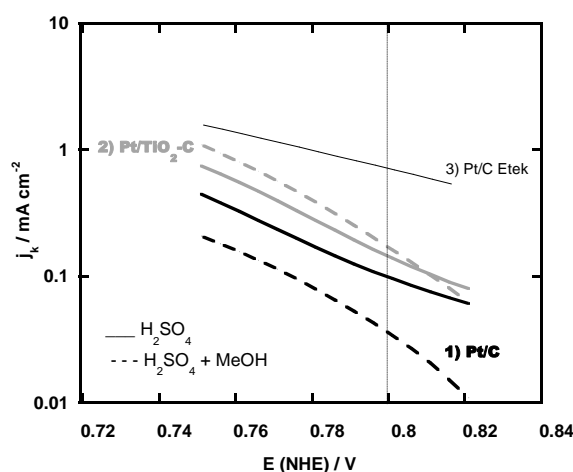


Fig. 5 ORR mass-corrected Tafel plots for the (1) Pt/C, (2) Pt/TiO₂-C and (3) Pt/C-Etek electrocatalysts calculated from the data (mass transfer corrected) in Fig. 5 in (—) H₂SO₄ and (---) H₂SO₄ + MeOH

ORR mass-corrected Tafel plots for the Pt/C, Pt/TiO₂-C and Pt/C-Etek electrocatalysts calculated from the data (mass transfer corrected) in Fig. 4 are displayed in Fig. 5. For catalysts synthesized by CVD (Pt/C and Pt/TiO₂-C) continue curves were recorded in 0.5 M H₂SO₄ electrolyte, whereas discontinue curves were recorded in 0.5 M H₂SO₄ + MeOH. The Tafel slope (60-70 mV dec⁻¹) of Pt/C and Pt/TiO₂-C was not affect by different electrolyte. That means the kinetic for ORR is not perturbed by presence of methanol in solutions. However, the j-E characteristic of Pt/C is cathodic shifted by 66 μA cm⁻² at 0.8 V when the



electrolyte contained MeOH. This effect was not observed on the Pt/TiO₂-C sample, the current density remains at 0.8 V. This phenomenon is direct evidence that Pt supported on TiO₂-C is not affected by methanol presence. The Tafel plot of Pt/C Etek was obtained in 0.5 M H₂SO₄ for comparison purposes. In acid medium, the kinetic current density calculated at 0.8 V/NHE of platinum deposited on TiO₂-C (147 $\mu\text{A cm}^{-2}$) show an enhancement compared to Pt/C (100 $\mu\text{A cm}^{-2}$) electrocatalyst prepared with the same methodology (CVD). However, it is evident that in acid medium the commercial sample had the higher density current (728 $\mu\text{A cm}^{-2}$), but its activity is affected drastically by the presence of methanol, in the case of Pt/TiO₂-C sample, it exhibits more tolerance to the methanol to carry out the ORR, caused by thermal treatment during the synthesis method and the TiO₂ phase rutile in contact with Pt that modified the electronic surface to adsorb the methanol or intermediates formation during the methanol electrooxidation. For this reason in this work, it is necessary to increase the electrochemical activity of Pt/TiO₂-C sample obtained by CVD method.

4 Summary and perspectives

Pt/TiO₂-C and Pt/C catalysts with nanometer size of 3 nm were successfully synthesized by chemical vapor deposition. Cyclic voltammetry as well as the rotating disk electrode for the ORR measurements in presence in alcohols showed that the catalyst synthesized exhibited excellent methanol tolerance for to be used as cathode in a Direct Methanol Fuel Cells. Specifically Pt/TiO₂-C exhibit a higher electrochemical activity to ORR in presence of methanol compared to the ethanol tolerance. The changes in the electronic properties of Pt could be explained by the TiO₂ rutile phase content through its interaction metal-oxide (Pt-TiO₂) obtained by the thermal treatment and the low pressure to be subjected during the synthesis method. A protecting effect of TiO₂ towards Pt that avoid the adsorption of methanol and CO intermediates on the surface of Pt was observed.

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