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ORIGINAL PAPER

Effect of the TiO_2 content as support with carbon toward methanol electro-oxidation in alkaline media using platinum nanoparticles as electrocatalysts

**J. C. M. Silva · R. F. B. De Souza · G. S. Buzzo ·
E. V. Spinacé · A. O. Neto · M. H. M. T. Assumpção**

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Abstract Platinum nanoparticles supported on physical mixtures of Vulcan carbon and TiO_2 (Pt/(C+TiO_2)) were prepared by the borohydride method and tested for methanol electro-oxidation in alkaline media. X-ray diffraction (XRD) analyses showed peaks characteristic of Pt face-centered cubic (fcc) structure and peaks associated with TiO_2 and carbon. Transmission electron microscopy (TEM) images showed the Pt nanoparticles distributed preferentially over the TiO_2 support with average particle sizes between 5 and 6 nm. Cyclic voltammograms showed a decrease of Pt surface area with increasing TiO_2 load while linear sweep in the presence of methanol showed Pt/(C+TiO_2) (60:40) with the highest current density in accordance with chronoamperometry. The results were attributed to Pt-based nanoparticles on TiO_2 which show enhanced catalytic activities for methanol oxidation due to a metal-support interaction. Furthermore, TiO_2 is a semiconductor with low conductivity when compared to carbon. Thus, it is expected that an intermediate proportion of carbon and TiO_2 as substrate could improve the activity of Pt nanoparticles without substantial loss of conductivity, resulting in a synergic effect.

Keywords Pt/(C+TiO_2) electrocatalysts · Borohydride reduction · Methanol electro-oxidation reaction

Introduction

Fuel cells are one of the most promising power utilization ways for application in portable devices, vehicles, and small stationaries, and among the various types of fuel cells, proton exchange membrane fuel cells (PEMFC) possess a series of highly advantageous features such as a low operating temperature and sustained operation at high current density [1–3].

PEMFC have been receiving extensive attention recently, especially direct alcohol fuel cells, since the latter do not bring problems such as in production, purification, and storage when compared to fuel cells fed by hydrogen. Moreover, some alcohols such as methanol have high energy density (702.32 kJ mol^{-1}) and are really attractive because of abundance, low cost, and convenience in production [3–6].

In a direct methanol fuel cell, a methanol/water solution is directly supplied to the anode as the fuel while oxygen/air is supplied to the cathode as the oxidant. At the anode, methanol reacts with water, producing carbon dioxide, protons, and electrons [7]:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- + \text{heat} \quad (1)$$

After that, the protons migrate to the cathode through the polymer electrolyte, while electrons travel to the cathode through an external circuit where electric power is delivered [7].

In order to increase the reaction rate of methanol electro-oxidation, electrocatalysts are used. Up to now, Pt-based electrocatalysts have been considered the most promising electrode material for anodic reactions, such as the methanol

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J. C. M. Silva · R. F. B. De Souza · G. S. Buzzo · E. V. Spinacé · A. O. Neto · M. H. M. T. Assumpção (✉)
Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Av. Prof. Lineu Prestes, 2242 Cidade Universitária, 05508-900 São Paulo, São Paulo, Brazil
e-mail: monica_ucri@yahoo.com.br

oxidation reaction. For instance, an excellent dispersion of Pt nanoparticles and the supporting materials are essential for the catalyst to increase its electrocatalytic activity [4, 6].

Taking into account the supporting materials, carbon is a common choice for supporting nanosized electrocatalysts because of its large surface area, high electrical conductivity, corrosion resistance, high chemical stability, pore structure, and low cost. However, this inert material does not help electrocatalytic activities but serves only as mechanical support [6, 8–10].

Thinking of supports with electrocatalytic activities, just few studies have been reported in this regard, mostly using oxide materials as active or promoting support such as SnO_2, SnO_2-doped Sb (ATO), and WO_3 [6, 11–14]. However, among them, TiO_2 is chemically stable in both acidic and alkaline solutions, has shown high catalytic activity for the reduction of some small organic molecules, and has been widely studied for its special photoelectric properties [4, 15].

Moreover, recent studies have reported that TiO_2 electrode as the support of Pt has highly catalytic activity and CO tolerance for alcohol electro-oxidation owing to the synergistic effect between Pt nanoparticles and TiO_2 support [15–19]. Considering that electrocatalysts of Pt supported on carbon present some troubles such as (1) anode poisoning by intermediates, mainly CO, forming during methanol oxidation; (2) the high extent of methanol crossover through the Nafion®-type membranes which depolarizes the air cathode [20–22]; and (3) the corrosion of carbon in the presence of platinum at low potential [23], Pt nanoparticles supported on TiO_2 could be a good alternative to overcome the problems of the Pt/C electrocatalyst.

Nevertheless, when compared to carbon materials, TiO_2 has a lower surface area and electrical conductivity since it is a semiconducting material. In order to optimize the properties of the support material, considerable efforts have been devoted to combine metal oxides with carbon materials [24]. Additionally, another way to improve the alcohol oxidation is the use of alkaline media. It is known that at high pH values, the kinetics of alcohol deprotonation is favored [25], leading to more reactive species [26, 27]. Moreover, in alkaline media, poisoning is considered smaller when compared to that in acid media [28–30]; furthermore, the oxygen reduction reaction has the kinetics favored [29].

Aiming the development of supports with electrocatalytic activities that could overcome some problems of methanol oxidation reaction, this work describes the use of platinum electrocatalysts supported on a mixture of carbon and TiO_2 at different mass proportions (C/TiO_2: 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100), prepared by the borohydride method for methanol electro-oxidation in alkaline media. It is important to stress that this kind of work presents a new concept of triple junction structure to promote the performance of Pt electrocatalysts.

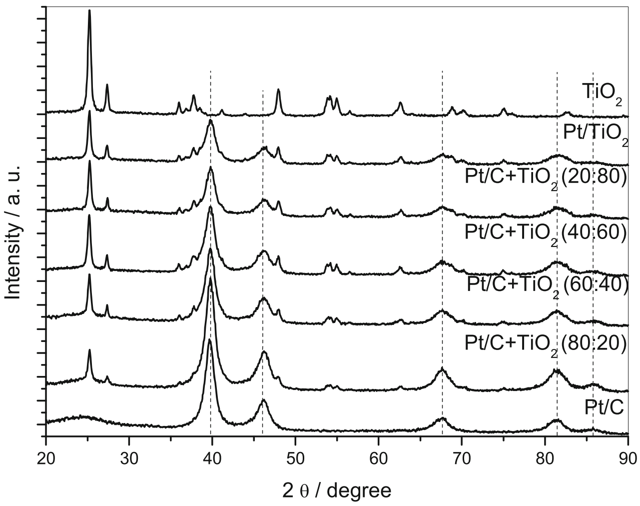


Fig. 1 X-ray diffractograms of the Pt/($C+TiO_2$) electrocatalysts prepared by the borohydride process. Pt (fcc) stressed in *dash line*

Materials and methods

The electrocatalysts of Pt/($C+TiO_2$) (20 % of metal loading) with C/TiO_2 mass ratios of 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100 were prepared by borohydride reduction [12, 31, 32] using $H_2PtCl_6 \cdot 6H_2O$ (Aldrich) as a metal source. According to this process, the supports (Vulcan XC72—Cabot Corporation and TiO_2—Degussa 2355) were dispersed in an isopropyl alcohol/water solution (50:50, *v*/*v*) and the mixture homogenized under stirring. After that, the metal source ($H_2PtCl_6 \cdot 6H_2O$) was added in an appropriate amount to obtain 20 % of metal loading and put on an ultrasonic bath for 5 min. Afterward, a solution of sodium borohydride dissolved in 5 mL of 0.1 mol L^{-1} KOH was added, in one portion, under stirring at room temperature, and the resulting

Table 1 Average crystallite size of the Pt/($C+TiO_2$) electrocatalysts prepared by the borohydride process

Catalyst	XRD	TEM	
	Average crystallite size (nm)	Mean diameter (nm)	Standard deviation (nm)
Pt/($C+TiO_2$) (100:0)	6	6.0	2.4
Pt/($C+TiO_2$) (80:20)	6	5.8	1.5
Pt/($C+TiO_2$) (60:40)	6	5.3	2.0
Pt/($C+TiO_2$) (40:60)	6	6.1	2.0
Pt/($C+TiO_2$) (20:80)	5	6.4	2.0
Pt/($C+TiO_2$) (0:100)	5	5.9	2.5

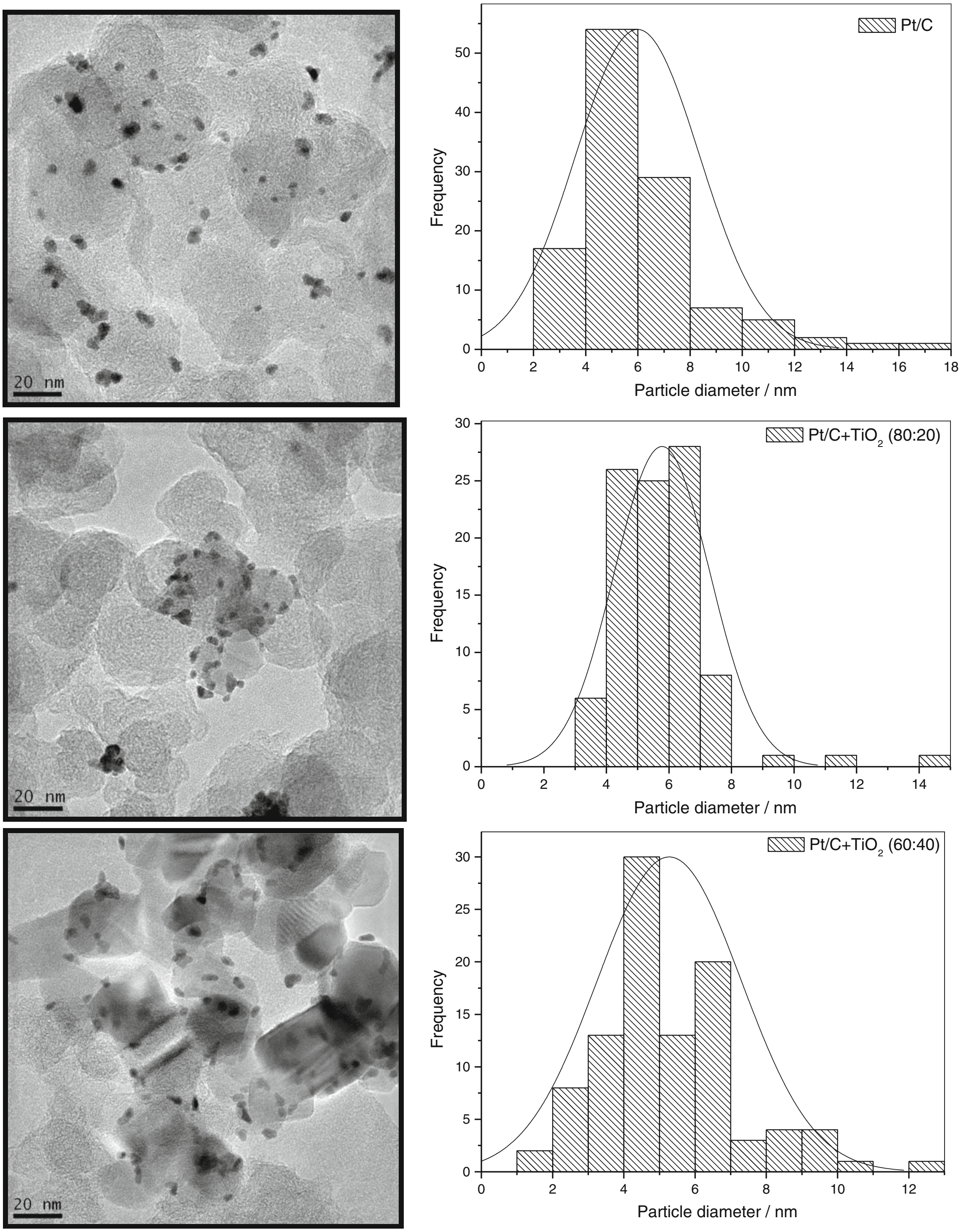


Fig. 2 TEM micrographs and histograms with the particle size distribution of the Pt/(C+TiO_2) electrocatalysts

solution was maintained under stirring for 15 min more. After this procedure, the final mixture was filtered and the solids washed with water and dried for 2 h at 70 °C.

The materials prepared were characterized by X-ray diffraction (XRD) using a Rigaku diffractometer (model Miniflex II) with a Cu Kα radiation source (0.15406 nm), the diffractograms being recorded in the range of 2θ=20° to 90° with a step size of 0.05° and a scan time of 2 s per step in order to obtain phases and estimate the average size of the nanocrystallites. Transmission electron microscopy (TEM)

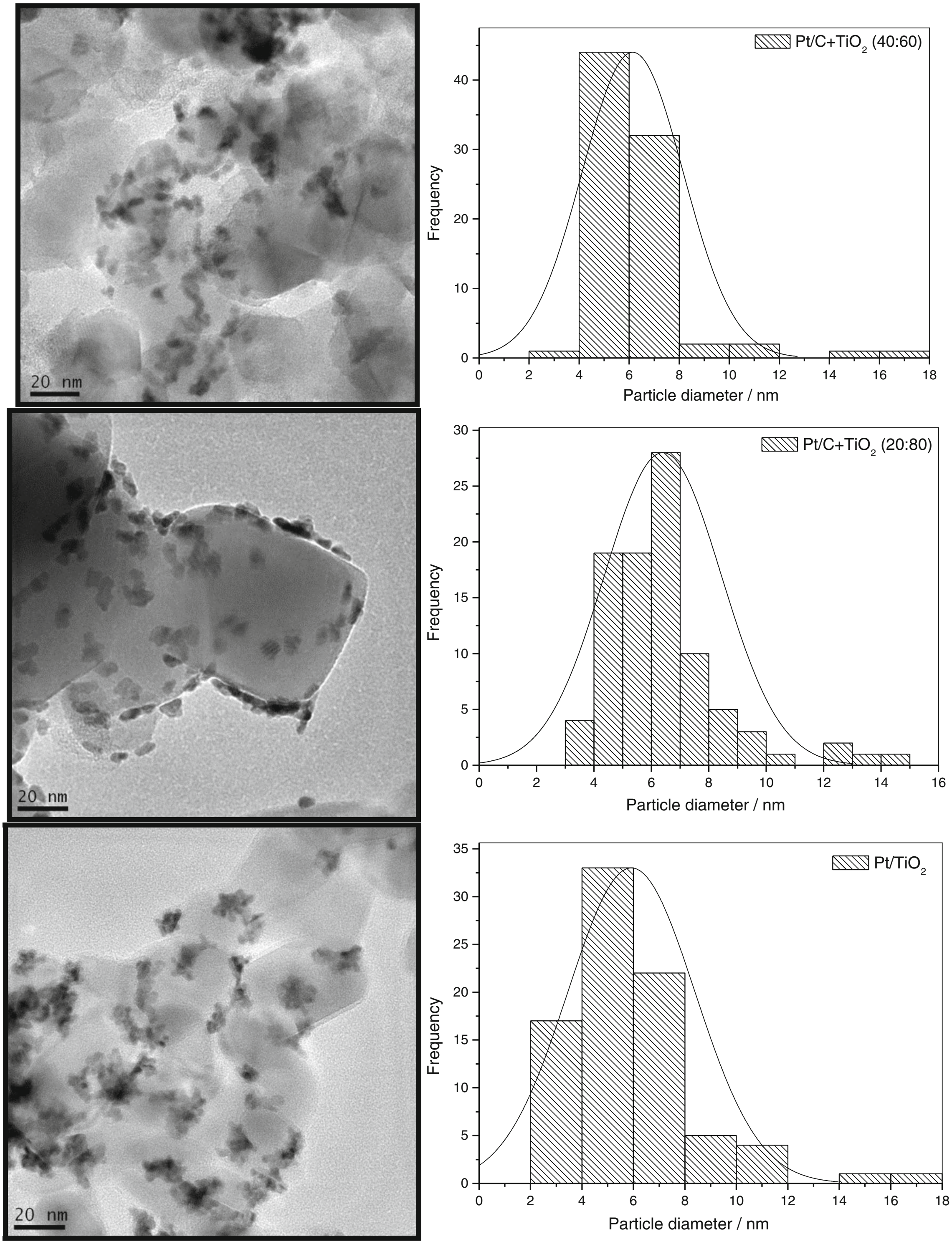


Fig. 2 (continued)

images were also carried out using a JEOL transmission electron microscope (model JEM-2100) operated at 200 kV to obtain the morphology, distribution, and average size of the nanoparticles which were determined by counting about 100 particles at different regions of the electrocatalysts prepared [33].

A potentiostat/galvanostat (PGSTAT 30) was employed for electrochemical measurements. A conventional three-electrode electrochemical cell was used. A platinum electrode and Ag/AgCl were used as the counter and reference electrodes, respectively. The work electrodes (geometric area of 0.5 cm^2 with a depth of 0.3 mm) were prepared using the thin

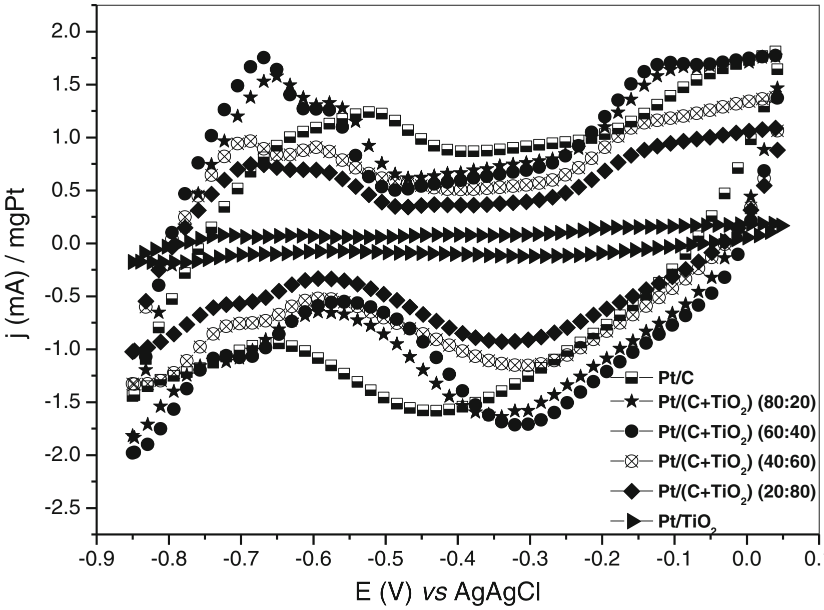


Fig. 3 Cyclic voltammograms of Pt/(C+TiO_2) electrocatalysts in 1 mol L^{-1} KOH saturated with N_2 at room temperature and scan rate of 10 mV s^{-1}

porous coating technique [34]. Characterizations were made by cyclic voltammetry conducted at a scan rate of 10 mV s^{-1} in 1 mol L^{-1} KOH aqueous solution in the presence and absence of 1 mol L^{-1} methanol, and the amperometric curves (*j-t*) were recorded in the same electrolyte containing methanol at −0.35 V for 1,800 s.

Results and discussion

From Fig. 1, it is possible to observe the XRD diffractograms of all electrocatalysts prepared with different C/TiO_2 mass ratios used as supports. All diffractograms showed five peaks associated with the Pt face-centered cubic (fcc) structure, according to JCPDF# 04-802 at 2θ=39°, 46°, 67°, 81°, and 86° which are related to the (111), (200), (220), (311), and (222) planes, respectively. TiO_2 materials showed peaks related to the anatase form, according to JCPDF# 84-1285 at 2θ= 25°, 37°, 48°, 54°, 55°, 62.5°, 70°, and 83° associated with the (101), (004), (200), (105), (211), (204), (220), and (206) planes, respectively, and also to the rutile form, according to JCPDF# 77-442 at 2θ=27.5°, 36°, 42°, 54°, and 69° related to the (110), (101), (111), (211), and (301) planes, respectively, as already observed before [35]. A broad peak relative to the

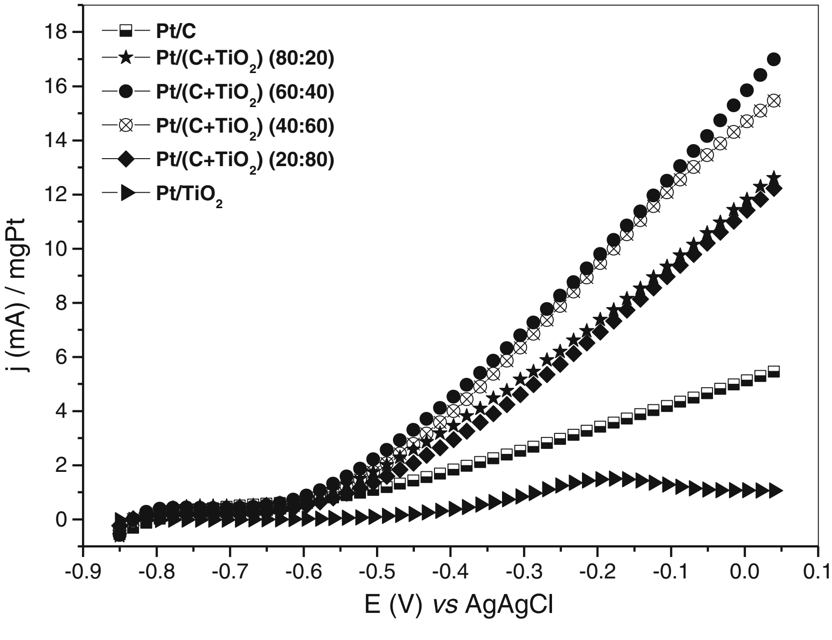


Fig. 4 Linear sweep of Pt/(C+TiO_2) electrocatalysts in the presence of 1 mol L^{-1} methanol and 1 mol L^{-1} KOH saturated with N_2 at room temperature and scan rate of 10 mV s^{-1}

carbon support was also observed at about 25° for the materials containing Vulcan XC72 carbon. The average crystallite sizes of platinum electrocatalysts were estimated using the Debye-Scherrer equation [36] and are shown in Table 1.

TEM micrographs and the histograms with the particle size distribution of each electrocatalyst studied are shown in Fig. 2. From this figure, it is possible to observe that in all materials with TiO_2 in the support, the Pt nanoparticles are preferentially anchored on TiO_2. However, heterointerfaces in the Pt/(C+TiO_2) catalysts, with Pt nanoparticles deposited on the boundaries of TiO_2 and on carbon of the C+TiO_2 substrate, were also observed. By TEM images, in all materials prepared, Pt nanoparticles are well dispersed on the support but some small agglomerations can be noted. Considering the histograms with the mean diameter of nanoparticles for all materials, most of the nanoparticles are in the range of 4–7 nm. Table 1 also contains the mean diameter size estimated from TEM images.

From Table 1, it is possible to observe that the mean diameter sizes of the catalyst particles estimated from TEM images are in accordance with XRD results and all electrocatalysts showed good and small average crystallite/nanoparticle size, around 6 nm, which is a characteristic of the reducing agent, sodium borohydride, since it enables good control of nanoparticle size and also composition [37].

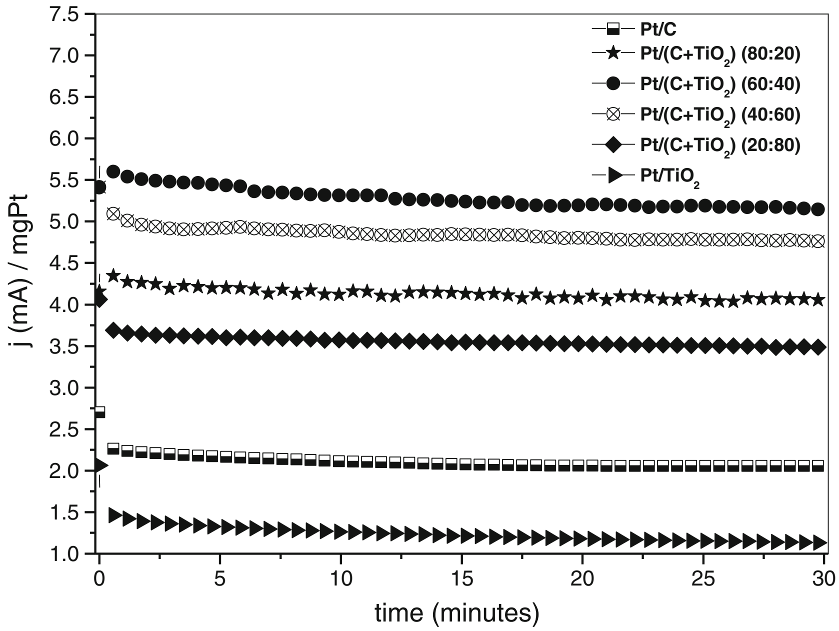
Electrochemical characterization was first done by measuring the cyclic voltammograms of all Pt/(C+TiO_2) catalysts in 1 mol L^{-1} KOH saturated with N_2 which are shown in Fig. 3. By Fig. 3, it is possible to observe a decrease in the voltammogram area with the TiO_2 addition, which can be explained by the lower conductivity of TiO_2 when compared to Vulcan carbon [38]. Furthermore, three characteristic regions of platinum electrocatalysts, i.e., hydrogen adsorption/desorption, double layer, and oxide formation/reduction regions, were also observed [39].

Linear sweep of Pt/(C+TiO_2) catalysts in the presence of 1.0 mol L^{-1} methanol and 1.0 mol L^{-1} KOH saturated with N_2 is shown in Fig. 4. From this figure, the highest electrocatalytic activity was obtained with Pt/(C+TiO_2) (60:40). It is known that Pt-based nanoparticles on TiO_2 support show enhanced catalytic activities for the methanol oxidation reaction due to a metal-support interaction [24]. Consequently, TiO_2 may provide a highly reactive oxygen species like OH to the active sites and promote CO oxidation [38]. Considering also that TiO_2 is a semiconductor material with low conductivity when compared to Vulcan carbon, it is reasonable to expect that an intermediate proportion of carbon and TiO_2 could improve the electrocatalytic activity of Pt nanoparticles toward methanol oxidation reaction without a significant decrease of conductivity, resulting in a synergic effect.

From the chronoamperometry results, in Fig. 5, the catalysts of Pt/(C+TiO_2) (60:40) and Pt/(C+TiO_2) (40:60) show the highest current density values. However, Pt/(C+TiO_2) (60:40) shows the highest current density, in agreement with Fig. 4. Considering that Pt/TiO_2 catalysts can oxidize CO more easily, it is expected that Pt/(C+TiO_2) could increase the electrocatalytic activity toward methanol oxidation reaction [40]. Furthermore, both materials, Pt/(C+TiO_2) (60:40) and Pt/(C+TiO_2) (40:60), present intermediate proportions of carbon and TiO_2 which could contribute to the increase in catalytic activity without a great decrease in conductivity.

From the same *j-t* curve, it is possible to observe that Pt/TiO_2 shows the lowest current density. This occurs since TiO_2 is a semiconductor material of which the electric conductivity is quite low for the conditions of the fuel cell operation, and

Fig. 5 Current-time curves at −0.35 V in the presence of 1 mol L^{-1} methanol and 1 mol L^{-1} KOH saturated with N_2 at room temperature



for the fuel cell operation, a high electric conductivity of the support is necessary in order to efficiently collect and transport electrons [38].

Conclusions

By the results obtained, it is possible to affirm that the borohydride reduction method is an efficient process to produce Pt/(C+TiO_2) electrocatalysts. In all electrocatalysts containing TiO_2, peaks attributed to the Pt fcc structure and TiO_2 in rutile and anatase forms were observed. TEM images showed the metal nanoparticles distributed preferentially over the TiO_2 support with average particle sizes between 5 and 6 nm for all catalysts. Electrochemical experiments for methanol oxidation reaction in alkaline media showed that the Pt/(C+TiO_2) (60:40) catalyst exhibited the highest current density, in accordance with the chronoamperometry results that also exhibited the Pt/(C+TiO_2) (60:40) as the best material for methanol oxidation. The results could be attributed to Pt-based nanoparticles on TiO_2 support which show enhanced catalytic activities for methanol oxidation reaction due to a metal-support interaction, and considering that TiO_2 is a semiconductor material with low conductivity when compared to Vulcan carbon, it is reasonable to expect that an intermediate proportion of carbon and TiO_2 could improve the electrocatalytic activity of Pt nanoparticles toward methanol oxidation reaction without a significant decrease of conductivity, resulting in a synergic effect.

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