

Enhanced Electrooxidation of Ethanol Using Pd/C + TiO₂ Electrocatalysts in Alkaline Media

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Abstract This work describes the use of Pd nanoparticles synthesized by the borohydride process and supported on physical mixtures of C + TiO₂ toward the ethanol electrooxidation reaction in alkaline media. In this study, the C/TiO₂ ratios were studied by ranging the mass proportions of C/TiO₂—100:0, 80:20, 60:40, 40:60, 20:80, and 0:100. X-ray diffraction patterns showed the presence of Pd face-centered cubic (fcc) structure, and carbon and TiO₂ in rutile and anatase phases. Transmission electron micrographs showed metal nanoparticles with average particle size between 5.5 and 7.2 nm for all electrocatalysts. Cyclic voltammograms of Pd/C + TiO₂ electrocatalysts showed a decrease of Pd surface area with the TiO₂ increasing, while the linear sweep and chronoamperometric results showed the Pd/C + TiO₂ (40:60) as the most promising electrocatalyst toward ethanol electrooxidation. The best results obtained with this catalyst were attributed to the presence of carbon and TiO₂ in intermediate proportions since TiO₂ supplies OH species and also changes the Pd d-band by a strong metal support interaction, increasing the alcohol oxidation without a significant decrease of conductivity and surface area.

Keywords Pd/C + TiO₂ electrocatalysts · Borohydride reduction · Ethanol electrooxidation reaction

Introduction

Alkaline direct ethanol fuel cell (ADEFC) has been attracting more attention among scientists due to the high specific

energy, low toxicity, and easiness of ethanol production from biomass as well as the ability of using non-platinum metals as electrocatalysts in alkaline media. However, the power output and the energy conversion efficiency are still low in practical use [1–4].

The main obstacle for the commercialization of ADEFC is the low kinetic of ethanol electrooxidation in low temperatures. Ideally, the complete oxidation of ethanol to CO₂ yields 12 electrons per ethanol molecule; however, it does not easily occur at moderate temperatures due to the difficulty of the C–C breaking bond, yielding instead of CO₂ products such as acetaldehyde or acetic acid liberating only two and four electrons, respectively, which greatly reduces the Faradaic efficiency of the fuel cell [4, 5].

Hence, many studies have been carried out to produce active electrodes for ethanol electrooxidation reaction mainly focused on Pt and Pt-based electrocatalysts supported on high surface area carbon materials [6–15]. However, it is known that carbon supports degrade over time due to electrochemical corrosion, causing the migration and also the agglomeration of Pt nanoparticles and, consequently, reducing the stability of these electrocatalysts. Thus, the use of different supports plays also an important role in ADEFC [1].

Taking into account the use of different supports, it is important to stress that three main characteristics are desirable: (i) large surface area for dispersion and stabilization of nanoparticles, (ii) good electrical conductivity to ensure efficient electron conduction, and (iii) stability in fuel cell operating environment [1, 16]. Considering these aspects, many substrates are being used such as carbon nanotubes [17–19], CeO₂ [20, 21], RhO₂ [21], Sb₂O₅·SnO₂ (ATO) [22, 23], and others [24, 25].

However, among the various materials indicated as support, TiO₂ has attracted much attention due to its high corrosion resistance in fuel cell working environment, stability in acid and alkaline solutions, low cost, high catalytic activity

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toward small organic molecule reduction, and special photoelectric properties [1, 13, 26–29]. Moreover, the strong metal support interaction (SMSI) between Pd and TiO_2 could also enhance the stability, catalytic activity, and CO poisoning tolerance [13, 30].

However, as TiO_2 is a semiconductor, with lower surface area and electrical conductivity in comparison with carbon materials, considerable efforts have been devoted to combine metal oxides, such as TiO_2 , with carbon materials [30]. Nakagawa et al. [4], for example, improved the kinetics and the selectivity of the electrooxidation of ethanol by using PtRu nanoparticles supported on a TiO_2 -embedded carbon nanofiber.

In this context, this work describes the electrooxidation of ethanol using Pd nanoparticles anchored on physical mixtures of carbon and TiO_2 as substrate (C/TiO_2). Pd was chosen because it is more abundant than Pt that could reduce the catalyst cost [31], and its electrocatalytic activity toward ethanol oxidation is remarkably higher than Pt in alkaline studies [3].

Materials and Methods

$\text{Pd}/\text{C} + \text{TiO}_2$ electrocatalysts (20 % of metal loading) with different C/TiO_2 mass ratios—100:0, 80:20, 60:40, 40:60, 20:80, and 0:100—were prepared by sodium borohydride method [23, 32, 33] using $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Aldrich) as metal sources as already described in previous papers [28, 34]. As support, we used physical mixtures of Vulcan XC 72 (Cabot Corporation) carbon and TiO_2 (Degussa 2355).

The $\text{Pd}/\text{C} + \text{TiO}_2$ electrocatalysts were characterized by X-ray diffraction (XRD) using a Rigaku diffractometer model Miniflex II using $\text{Cu K}\alpha$ radiation source (0.15406 nm). X-ray diffraction patterns were recorded in the range of $2\theta = 20^\circ$ – 90° with a step size of 0.05° and a scan time of 2 s per step. Transmission electron microscopy (TEM) images were also performed using a JEOL microscope model JEM-2100 operated at 200 kV.

Electrochemical experiments were also carried out using cyclic voltammetry (CV) and chronoamperometry (CA) at room temperature using a potentiostat/galvanostat PGSTAT 30 Autolab. In these measurements, a conventional cell composed of three electrodes was employed: The working electrodes (geometric area of 0.5 cm^2 with a thickness of 0.3 mm) were prepared using the thin porous coating technique [35], the reference electrode was an Ag/AgCl ($\text{KCl } 3 \text{ mol L}^{-1}$) homemade electrode, and the counter electrode was a Pt plate. The ethanol electrooxidation was studied in a 1 mol L^{-1} KOH and also in the presence of 1 mol L^{-1} ethanol solution saturated with N_2 .

Results and Discussion

Figure 1 shows XRD for all $\text{Pd}/\text{C} + \text{TiO}_2$ electrocatalysts prepared with different C/TiO_2 mass ratios. In all XRD patterns, peaks at $2\theta = 39^\circ$, 46° , 68° , and 82° which respectively correspond to (111), (200), (220), and (311) reflections of Pd face-centered cubic (fcc) crystal according to JCPDF# 88–2335 were observed as already evidenced by other authors [36–38]. Furthermore, TiO_2 materials show peaks associated to the anatase form at $2\theta = 25^\circ$, 37° , 48° , 54° , 55° , 62.5° , 70° , and 83° associated with the (101), (004), (200), (105), (211), (204), (220), and (206) planes according to JCPDF# 84–1285 and also to the rutile form at $2\theta = 27.5^\circ$, 36° , 42° , 54° , and 69° associated with the (110), (101), (111), (211), and (301) planes according to JCPDF# 77–442 as already observed before [28, 34, 39].

TEM images were also obtained in order to analyze the nanoparticle distribution on the support and the nanoparticle mean distribution which were estimated by counting about 100 randomly chosen particles from different and relevant TEM images [40, 41]. Figure 2 shows the images for each electrocatalyst in study and also its histograms with the nanoparticle size distribution and the mean diameter. From Fig. 2, it is possible to observe that the Pd nanoparticles are dispersed on the substrate although some agglomerates can be observed. The mean nanoparticles size obtained is between 5.5 and 7.2 nm, as expected, since the borohydride reduction process yields nanoparticles with good control of nanoparticle size [42].

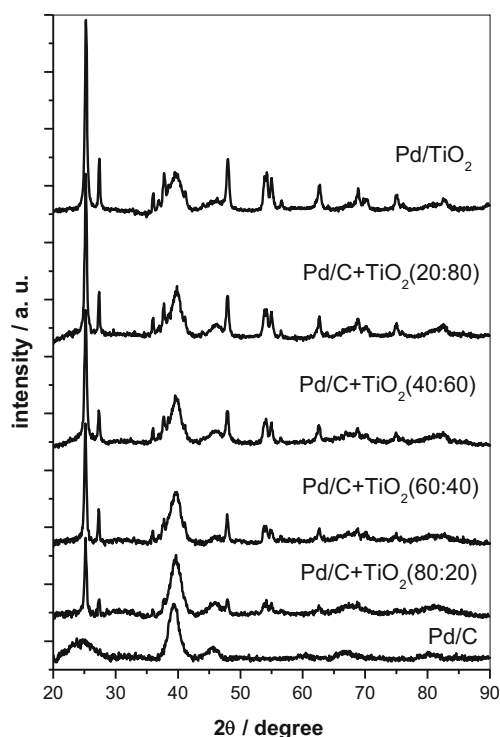


Fig. 1 X-ray diffraction patterns of the $\text{Pd}/\text{C} + \text{TiO}_2$ electrocatalysts

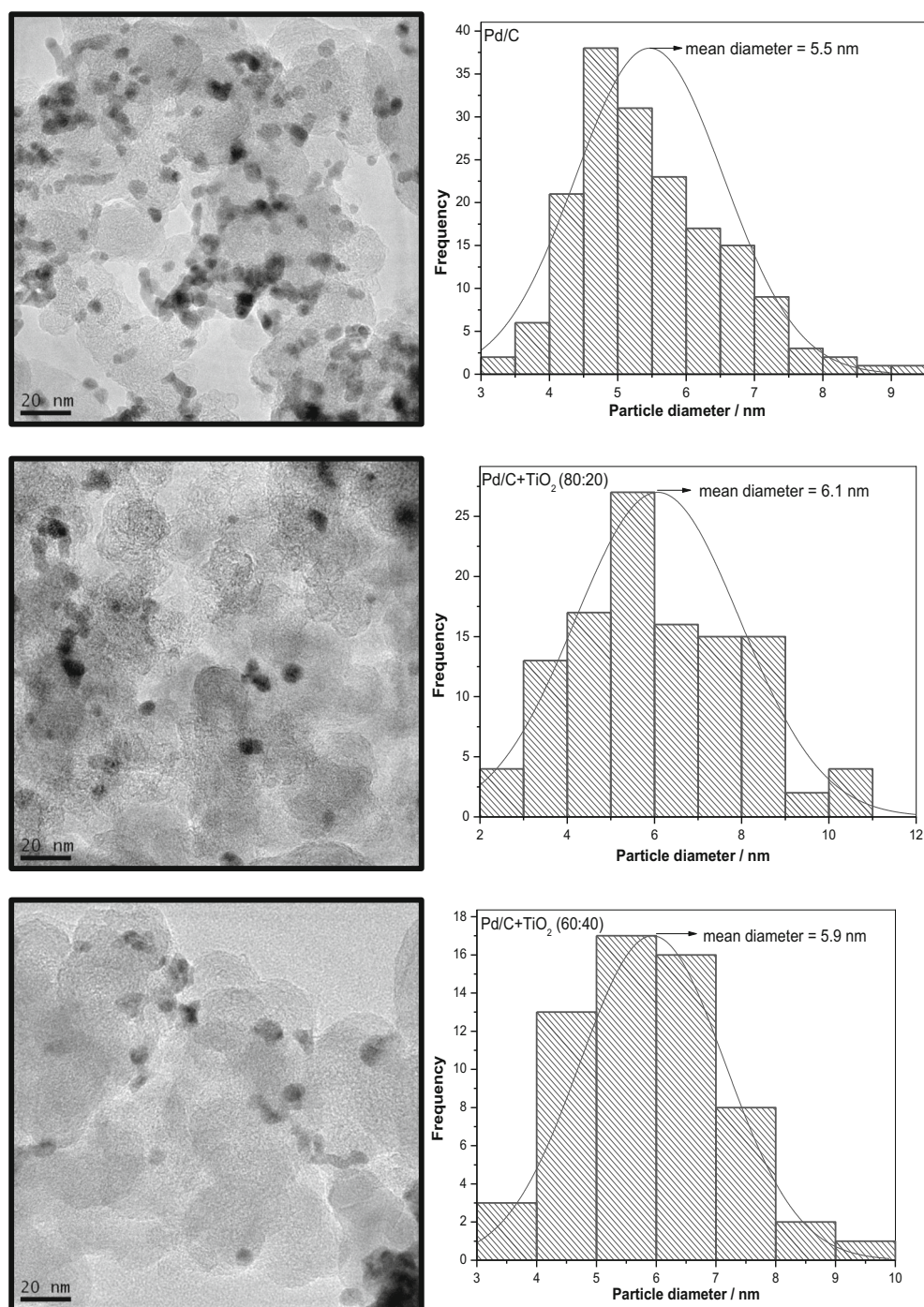


Fig. 2 TEM images of the Pd/C + TiO₂ electrocatalysts (*left side*) and its histograms with the particle size distribution of each material studied (*right side*)

Electrochemical experiments were first conducted by cyclic voltammetry in KOH 1 mol L⁻¹ saturated with N₂ and at room temperature (Fig. 3). By these results, one can observe a decrease in the voltammogram area with the TiO₂ load, as expected, since TiO₂ is a semiconductor with lower conductivity than Vulcan carbon [16]. This observation was also found in previous studies. Furthermore, in all voltammograms, the three characteristic regions of Pd electrocatalysts

were observed: hydrogen adsorption/desorption, double layer, and oxide formation/reduction [43].

Figure 4 shows the linear voltammetry in presence of 1 mol L⁻¹ ethanol. By this figure, the most promisor electrocatalyst was Pd/C + TiO₂ (40:60) since it presented the highest current normalized by Pd loading in the ethanol electrooxidation reaction. Considering previous experiments with Pt/C + TiO₂ [28, 34], intermediate proportions of TiO₂

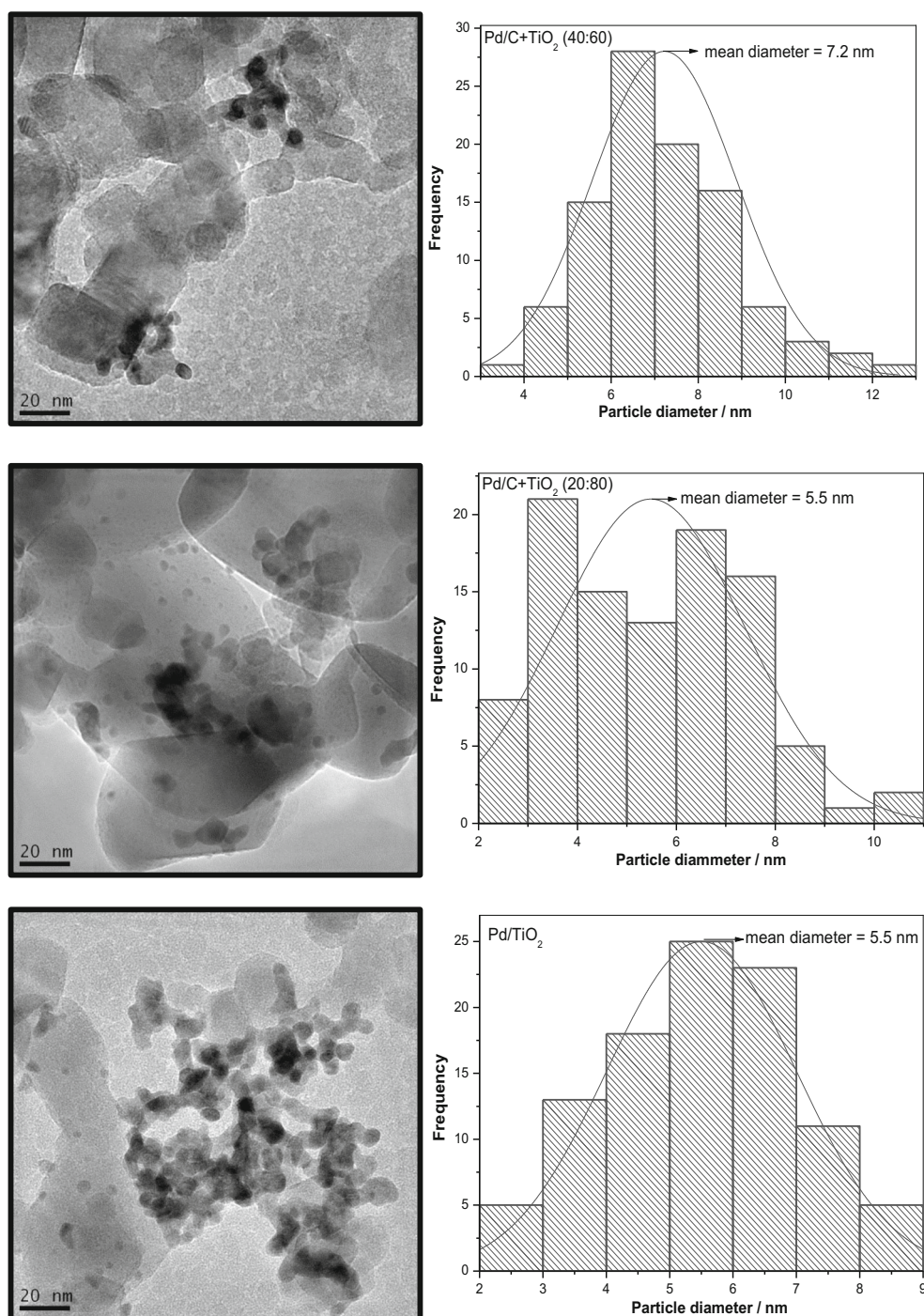


Fig. 2 (continued)

and carbon as substrates resulted in higher electrocatalytic activity toward alcohol oxidation, since TiO₂ could provide oxygenated species and change the Pt electron density, without an extreme reduction of area, since there is approximately half of the substrate composed of carbon with high superficial area [16, 30, 44].

Additionally, Nakagawa et al. [4] generated a two times higher electric power with a quarter of the PtRu loading by

using PtRu nanoparticles supported on a TiO₂-embedded carbon nanofiber toward ethanol electrooxidation. In this work, they achieved that the best ratio of Ti/C was 1; in other words, intermediate proportions of carbon and Ti were achieved to be the best, as already mentioned in our previous study [28, 29] and as observed in the present study.

Taking into account chronoamperometric results obtained in KOH 1 mol L⁻¹ and ethanol 1 mol L⁻¹ (Fig. 5), once more,

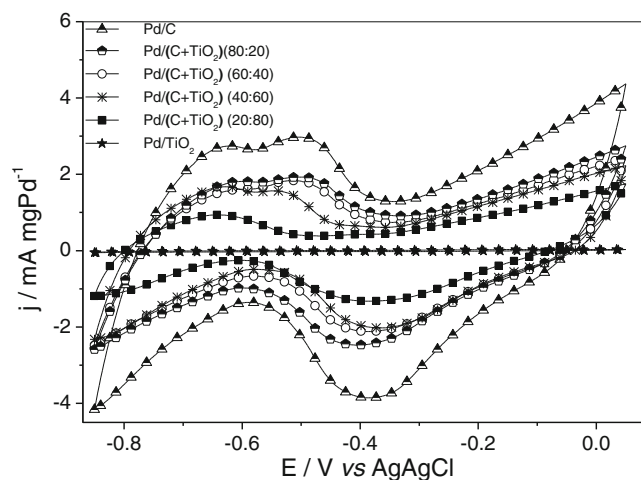


Fig. 3 Cyclic voltammograms of Pd/C + TiO₂ electrocatalysts in 1 mol L⁻¹ KOH saturated with N₂ and at scan rate of 10 mV s⁻¹

the Pd/C + TiO₂ (40:60) showed to be the most promising electrocatalyst since it presented the highest current normalized by Pd loading during 30 min with also a good stability (without a higher decrease of current during the 30 min). The Pd/C + TiO₂ (40:60) showed a current normalized by Pd loading 30 % higher when compared to Pd/C.

It is well known that the support influences the catalytic activity of the supported metal particles although the nature of this interaction remains unclear. Generally, the changes in catalytic activity are described as a modification of the electronic properties of the metal particles induced by a metal-support interaction, and several modes have been proposed [45]. Additionally, it is also known that TiO₂ manifest SMSI with VIII group of transition metals (e.g., Pd, Pt, Ni, and Ir) [46, 47].

Thus, the improvement in current normalized by Pd loading obtained with Pd/C + TiO₂ (40:60) can be explained as a result of the TiO₂ introduced in intermediate proportions with

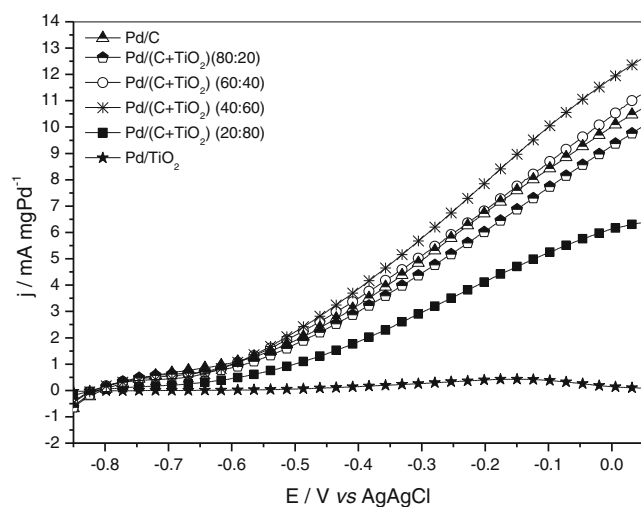


Fig. 4 Linear sweep Pd/C + TiO₂ electrocatalysts in presence of 1 mol L⁻¹ ethanol and at scan rate of 10 mV s⁻¹

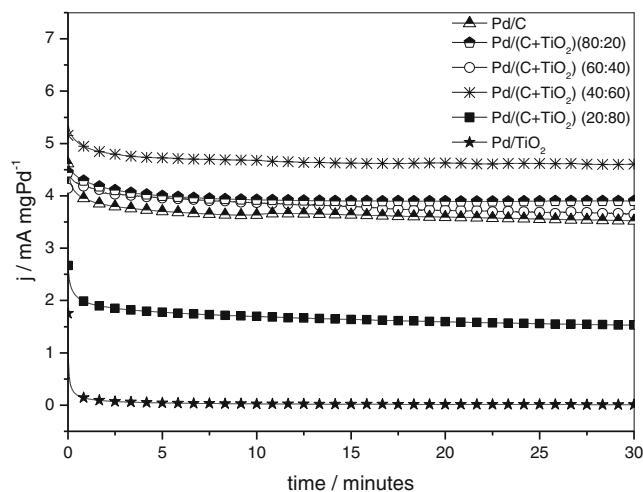


Fig. 5 Current-time curves of the Pd/C + TiO₂ electrocatalysts at -0.35 V in presence of 1 mol L⁻¹ ethanol

carbon as substrates since TiO₂ can work not only as substrate but also as a co-catalyst support, providing oxygenated species and shifting the d-band of the Pd nanoparticles leading to weak interactions between Pd and intermediate species, changing also the Pd chemisorptive properties, which are normally obtained using the second metal in the conventional Pt-M system. [16, 30, 44, 47, 48].

Among all electrocatalysts in study, just Pd/C + TiO₂ (20:80) and Pd/TiO₂ showed current normalized by Pd loading lower than the Pd/C. This result can be associated with the reduction in the conductivity by the presence of TiO₂ in higher amounts and also with the reduction of superficial area. However, the other electrocatalysts—Pd/C + TiO₂ (40:60), Pd/C + TiO₂ (60:40), and Pd/C + TiO₂ (80:20)—showed higher current normalized by Pd loading than Pd/C; nevertheless, the Pd/C + TiO₂ (40:60) and Pd/C + TiO₂ (60:40) present the highest ones.

In conclusion, probably the SMSI manifested more intensity on electrocatalysts with intermediate proportions of carbon and TiO₂ since there is a modification of the Pd d-band and the supply of OH species without a significantly reduction of area and conductivity.

Conclusions

Among all electrocatalysts in study, Pd/C + TiO₂ (40:60), Pd/C + TiO₂ (60:40), and Pd/C + TiO₂ (80:20) showed higher current normalized by Pd loading than Pd/C. In these electrocatalysts, there was the introduction of TiO₂ without a higher decrease of conductivity and superficial area. Considering that, among all electrocatalysts in study, Pd/C + TiO₂ (40:60) showed the highest current normalized by Pd loading, it is possible to affirm that intermediate proportions of carbon and TiO₂ as substrates could contribute for the ethanol

oxidation reaction since the TiO_2 works as a co-catalyst, providing oxygenated species and shifting the d-band of the Pd nanoparticles (SMSI) leading to weak interactions between Pd and intermediate species and consequently favoring the ethanol oxidation reaction.

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