

Use of commercial TiO₂ as direct ethanol fuel cell electrocatalyst support

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Abstract. Direct ethanol fuel cells (DEFCs) are efficient converters of chemical energy into electrical energy. DEFCs operate at low temperatures, and an anode, a cathode and an electrolyte are the main constituents. In alkaline media, electrocatalysts, responsible for promoting anodic and cathodic reactions, are generally composed of palladium supported on carbon black. Other materials have been studied in order to make the ethanol oxidation reaction (EOR) more efficient. In this work, the effect of commercial TiO₂ as alternative support to Pd-based catalysts for the EOR was evaluated. The synthesized materials were characterized by X-ray diffraction, linear voltammetry and chronoamperometry, aiming to determine the effect of different supports on the performance of the EOR.

Key words

Direct ethanol fuel cell, TiO₂ catalyst support, Pd-based electrocatalyst, ethanol electrooxidation reaction.

1. Introduction

Fuel cells are high power density systems, small and lightweight. They can be operated at low-temperature, and there is a large range of applications to be explored. An electrolyte separates the anode (where the fuel is supplied) from the cathode (in which oxygen or air is supplied). The most common fuel is hydrogen, but methanol and ethanol have been studied as promising alternatives, specially regarding to mobile applications. Ethanol, specifically, is an attractive alternative due to its non-toxicity, low cost, ease of transportation and storage. Moreover, it is a biofuel, product from the fermentation of biomass [1].

However, the ethanol oxidation reaction (EOR) is a low kinetic process; therefore, a catalyst is needed. Platinum supported on carbon is the most used catalyst material in fuel cells, but due to Pt elevated price, poisoning by carbon monoxide (a byproduct of alcohol oxidation) and

carbon support degradation over time, other materials have been studied. Palladium belongs to the same periodic table group, presents atomic size similar to Pt and the same crystal structure. It is more abundant on Earth, consequently its price is lower. In addition, it has been reported that Pd presents higher electrocatalytic activity than Pt in alkaline media regarding the EOR [2].

Carbon-based materials have been extensively studied as palladium catalysts support, and recently TiO₂ has been employed due to its stability and good electrical conductivity [3]. In addition, it can work not only as a support but also as a co-catalyst to the ethanol oxidation reaction [2].

Besides, Liu et al. [4] reported a low absorption of ethanol oxidation byproducts on the electrode surface, caused by a high dispersion ratio between the metal and the TiO₂, inducing an excellent performance. T. Wu *et al.* [3] have proposed complex TiO₂ synthesis routes, including nanotube structures, aiming to obtain a support with ideal features. The objective of the present work is to evaluate the commercial AEROXIDE® TiO₂ P25 performance as Pd electrocatalyst support.

2. Experimental

A. Catalyst synthesis

To obtain Pd supported on TiO₂, ethylene glycol was used as a reduction agent and AEROXIDE® TiO₂ P25 as support. Initially, a solution containing the precursor salt (PdCl₂) was prepared in ethylene glycol and water, then TiO₂ was added and the dissolution of the salts was completed in an ultrasonic bath. The solution was maintained at 35 °C, under reflux and agitation to enable the metals reduction. The catalysts were washed and dried. For comparison purposes, all synthesis were

repeated using the carbon Vulcan XC72R as support. The electrocatalyst electrochemical behaviour and structure were evaluated.

B. Structural characterization

The X-ray analysis were performed at a Phillips diffractometer, model X'Pert MDP with Cu-K α radiation.

C. Electrochemical characterization

In order to determine the electrochemical activity, linear voltammetry and chronoamperometry were performed in 1 M ethanol and 1 M NaOH, N₂ purged during 20 minutes before the analysis, at 25 °C. The measurements were carried out in an AUTOLAB PGSTAT302N potentiostat, in a three-electrode cell, with platinum as counter electrode and Hg/HgO as reference electrode. A graphite disc was used to support the working electrode, covered by a 238 μ L layer of a mixture composed by 12 mg of catalyst, 2 mL of ethanol (Merck) and 25 μ L of Nafion® solution (5%, Aldrich). The current was normalized by Pd loading (40 wt%). The linear voltammetry was performed at a scan rate of 10 mV.s⁻¹, in a range between -0,9 V and 0.05 V. Stability of Pd/C and Pd/TiO₂ was tested by chronoamperometry for 3600 s at the onset potential, -0,7 V.

3. Results and Discussion

A. X-ray diffraction

The diffractograms for the TiO₂ support and Pd/C and Pd/TiO₂ electrocatalysts are shown in Figure 1. The highlighted peaks correspond to different Pd reflection planes (JCPDS 05-0681), and evidence the reduction of the metal on the supports. The other peaks are related to the TiO₂ crystalline structure.

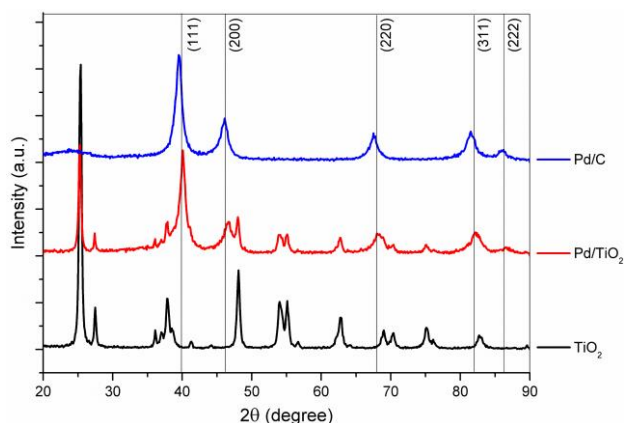


Fig. 1. X-ray diffraction patterns of the TiO₂ support and Pd/C and Pd/TiO₂ electrocatalysts.

Data from diffraction peaks were employed in calculations to estimate the particle sizes, using the Scherrer equation [5]:

$$D = (k \times \lambda) / (FWHM \times \cos \theta) \quad (1)$$

When supported in carbon, Pd nanoparticles exhibited an average particle size of 9 nm, while the particles supported on TiO₂ presented an average particle size of 10 nm, similar to what is presented in the literature [6][7].

B. Linear Voltammetry

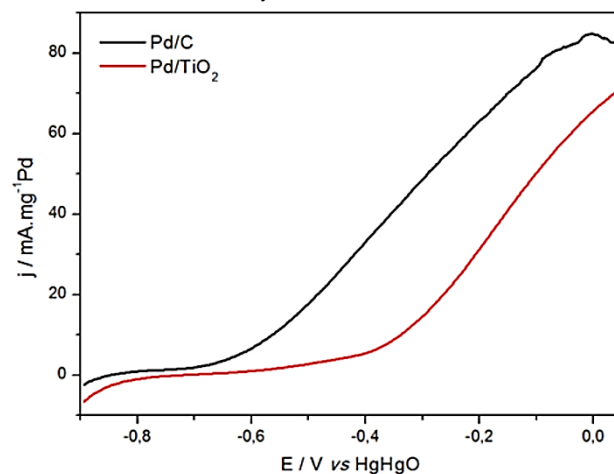


Fig. 2. Linear voltammograms of the Pd/C and Pd/TiO₂ electrocatalysts in 1 M NaOH and 1 M ethanol at a scan rate of 10 mV.s⁻¹.

Figure 2 exhibits the linear voltammograms corresponding to each synthesized catalyst. Even though Pd supported on carbon (Pd/C) presented higher current densities, the results regarding the catalyst supported on TiO₂ (Pd/TiO₂) present similar behaviour. J. C. M. Silva *et al* [2] used TiO₂ (Degussa 2355) and observed a reduced current density for Pd/TiO₂ in comparison to carbon.

However, contrary to what has been reported in the literature, in the present work it was possible to verify that the use of commercial TiO₂ achieved results similar to those presented by Pd supported in Vulcan, evidencing the importance of the characteristics of the TiO₂ support, which may influence the dispersion of particles on the surface of the support and consequently the active surface area.

C. Chronoamperometry

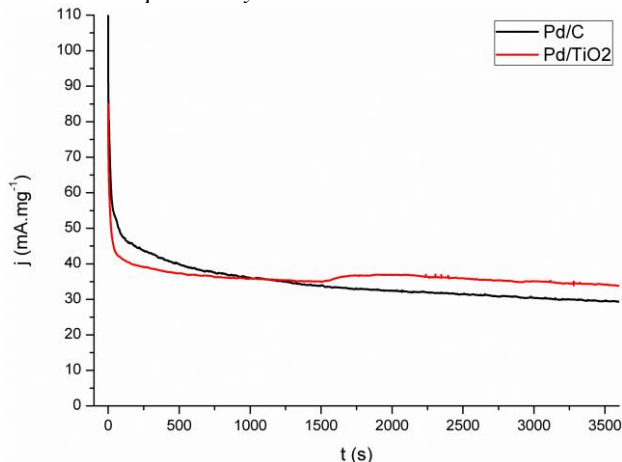


Fig. 3. Chronoamperometry of the Pd/C and Pd/TiO₂ electrocatalysts in 1 M NaOH and 1 M ethanol at -0,7 V.

The chronoamperometric measurements were used to investigate the stability of the catalysts [8]. A loss of 50% of the initial current density was observed after 34 s in the Pd/C catalyst, while the Pd/TiO₂ lasted 56 s. The lower initial current density, less abrupt drop and higher stability current indicate a lower degradation rate for the Pd/TiO₂ catalyst [9][10]. After 30 min operation, very slow decline was observed on both catalysts. This suggests that TiO₂ is a stable substitute to carbon as supports in DEFCs [5].

4. Conclusion

Commercial TiO₂ can be used as support for Pd, exhibiting performance similar to carbon support (Vulcan). However, the TiO₂ characteristics may vary [2] and this affects the electrocatalytic activity.

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