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Oxygen Reduction Reaction on Pt-ZrO$_2$/C during the Alcohol Crossover in Experimental Direct Alcohol Fuel Cells

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Abstract: *Pt–ZrO$_2$/C composite was synthesized by chemical reduction process. ZrO$_2$ precursor was obtained by sol-gel at room temperature. The synthesis allowed the formation of Pt-ZrO$_2$/C nanoparticles. The nanoparticles were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and transmission electron microscopy (TEM) techniques. The electrochemical experiments were carried out for investigating the electro-catalytic properties of the synthesized composite to promote the cathodic reaction in direct alcohol fuel cells (DAFC). The results indicated that Pt-ZrO$_2$/C showed more tolerance than Pt/C based electrocatalyst to the presence of methanol or ethanol (due to alcohol crossover) during the oxygen reduction reaction (ORR) in direct alcohol fuel cells. The experimental results indicated that the ORR on Pt-ZrO$_2$/C composite was predominant by the four electron transfer mechanism and first order reaction. The Pt-ZrO$_2$/C based electrocatalyst showed adequate performance to carry out the ORR in experimental direct alcohol fuel cells operating at room temperature. The results revealed that Pt-ZrO$_2$/C composite could be considered as a suitable candidate for reducing oxygen on the cathode of experimental DAFCs.*

Keywords: oxygen reduction reaction, alcohol fuel cell, Pt-ZrO, nanoparticles

1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFC) and more specifically, the direct alcohol fuel cells (DAFC) have been recognized as promising devices for producing clean electric energy due to their high chemical to electrical conversion efficiency and low emissions. DAFCs can be considered in a near future, the electric supply systems of portable electronic devices at room temperature and with a liquid fuel, i.e. methanol or ethanol [1-4]. Platinum based alloys are mainly used to carry out the redox reactions occurring at the DAFC [5-7]. High cost and poisoning of the main electrocatalyst used in the cathode of this kind of fuel cell is the challenge to be overcome as the first step to industrialize the direct alcohol fuel cells for commercial applications. The high cost is due to the existence of Pt as the base of cathodic electrocatalysts in the fuel cells to promote the oxygen reduction reaction (ORR) with 4 electrons and produce H_2O. The poisoning effect of the Pt based cathodic electrocatalysts is due principally to the presence of alcohol from the anode of the cell by the very well known process: alcohol crossover [8,9]. ORR is also the limiting reaction in a DAFC due to the slow velocity to produce water via 4 electrons or 2 electrons assisted by H_2O_2, and nowadays, this implication has determined the use of Pt as the main electrocatalyst to carry out this reaction still in the most promising experimental direct alcohol fuel cells [10-13].

Nowadays the research about the synthesis and characterization of new and low cost materials for catalyzing the cathodic reaction in a DAFC is focused in the development of better kinetic characteristics than conventional Pt based electrocatalysts used in this kind of fuel cells. Some interesting characteristics of novel electrocatalysts are associated with faster processes to perform the oxygen reduction reaction with 4 electrons, as well as the possibility to obtain materials with high tolerance to alcohol crossover from the anode that could avoid the formation of a mixed potential to carry out the oxygen reduction reaction in the cathode, resulting in a better fuel cell performance [14,15].

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Pt alloys have been extensively investigated for cathodic reactions in DAFCs, and some of the most interesting results of Pt based electrocatalysts have been discussed with the use of transition metals like V [16], Co [17,18], Fe [19,20], Ni [21,22]. The preparation of Pt-metal oxide composites supported on carbon (Pt-MO_x/C) has recently taken a great interest by the scientific community due to promising results in the field of heterogeneous catalyst associated with direct alcohol fuel cells. It was previously discussed that some metal oxide composites (SnO_2, WO_3, CeO_2, ZrO_2) in presence of Pt have the possibility of performing the oxygen reduction reaction and probably those composites could help to diminish the content of Pt as the active electrocatalyst in the electrodes of DAFCs [23-26]. Pt-ZrO_2 based nanometric metal oxide composite is able to form mesoporous sites where the active electrocatalyst can be uniformly distributed on the ZrO_2 matrix for improving the active surface area and consequently it is possible to observe an increase of the current density at the oxygen reduction reaction. ZrO_2 shows good thermal and chemical stability, it can be synthesized by several methods including experimental techniques at room temperature and the material can crystallize in monoclinic, cubic, tetragonal and amorphous structures [27-31]. ZrO_2 is an amphoteric oxide with adequate properties to be used in redox reactions of DAFCs.

In this work Pt-ZrO_2/C was prepared in two steps by sol-gel of ZrO_2 and chemical reduction of metallic Pt salt. The metal oxide composite was supported on activated carbon during the reduction process. The good interaction between the composite phases showed good electrochemical response to carry out the oxygen reduction reaction in presence of methanol and ethanol (alcohol crossover). Pt-ZrO_2/C based electrodes were used in experimental direct alcohol fuel cells (methanol and ethanol) and the cells were tested during 60 h to corroborate the tolerance to alcohol crossover in the cathodic reduction reaction of the fuel cells.

2. EXPERIMENTAL

2.1. Preparation of Pt-ZrO_2/C electrocatalyst

Pt-ZrO_2 electrocatalyst was prepared in two steps: (i) Synthesis of precursor ZrO_2 by sol-gel and (ii) chemical reduction process of Pt metallic salt.

2.1.1. Preparation of ZrO_2 precursor

ZrO_2 nanoparticles were synthesized by sol-gel method. 0.2 M zirconium (IV) oxychloride octahydrate ($ZrOCl_2.8H_2O$) from Sigma Aldrich was hydrolyzed by adding dropwise ammonium hydroxide (NH_4OH, 30% v/v) at constant stirring to obtain a pH value of 10. The hydrolysis process was aged at room temperature for 3 h to complete the gel formation of $Zr(OH)_4$. The sol-gel chemical reaction for obtaining $Zr(OH)_4$ was:

$$ZrOCl_2 + 2NH_4OH + H_2O \rightarrow Zr(OH)_4 + 2NH_4Cl \quad (1)$$

The gel was then filtered and washed several times to remove residual Cl^- from the precursor. The $Zr(OH)_4$ was dried at 110 °C for 12 h. A calcinations process in air at 600 °C for 2 h was done to obtain ZrO_2 powder. The chemical conversion process from $Zr(OH)_4$ to ZrO_2 can be described according to the dehydroxylation reaction:

$$Zr(OH)_4 \rightarrow ZrO_2 + 2H_2O \quad (2)$$

2.1.2. Synthesis of Pt-ZrO_2/C

Vulcan XC-72R carbon was used as support for the electrocatalytic composite. The surface chemistry of the carbon was modified by oxidation process in liquid phase to assure the dispersion of Pt nanoparticles on mesoporous ZrO_2. Vulcan carbon was dispersed in an aqueous solution containing HNO_3 at 65% v/v. The mixture was refluxed for 12 h at 85 °C at constant stirring for creating oxygen functional groups on the carbon surface. Functionalized carbon was filtered, washed with deionized water and the sample was dried at 200 °C in air for 12 h.

The Pt-ZrO_2 electrocatalyst supported on carbon was synthesized at 1:1 molar ratio (Pt:ZrO_2) and the electrocatalytic loading of Pt-ZrO_2 on carbon was 10%. The composite was prepared by chemical reduction of chloroplatinic acid hydrate ($H_2PtCl_6{\cdot}xH_2O$) obtained from Aldrich and dissolved in ethylene glycol. This organic material was used as solvent and reducing agent. The solution was maintained under stirring (500 RPM) for 2 h at room temperature to obtain a homogeneous mixture. The mixture was then refluxed at 197 °C for 30 min. The color of the refluxed solution changed from light orange to dark brown, indicating the formation of Pt nanoparticles. The colloidal solution obtained from the synthesis of Pt nanoparticles was placed in a round bottom flask and then the ZrO_2 powder and functionalized carbon were incorporated at the same time and immediately the solution was vigorously stirred at room temperature for 2 h. The Pt-ZrO_2/C electrocatalyst was filtered and washed with deionized water before applying a thermal treatment in a tubular furnace under nitrogen atmosphere at 500 °C for 2 h.

2.2. Characterization of the synthesized electrocatalyst

The structural analysis of the electrocatalytic composite was done using an x-ray diffractometer Rigaku DMAX 2200 (CuKα radiation, λ=0.154 nm) and the software Jade 6.5. The superficial area analysis was carried out by BET technique and the pore size distribution was measured by BJH method (adsorption/desorption isotherms). An electron transmission microscope JEOL-2200FS (200 kV) was used to investigate the nature of Pt-ZrO_2/C nanoparticles.

The electrochemical characterization of the synthesized material was focused on the oxygen reduction reaction in aqueous solution. A solartron (potentiostat-galvanostat 1287/1260) was used to carry out the experiments at room temperature. A rotating disc electrode (0.071 cm^2) was used as working electrode and O_2 saturated 0.5M H_2SO_4 was used as the electrolyte. The linear voltammetry studies were performed at a scan rate of 5 $mV{\cdot}s^{-1}$. The ORR on the electrocatalytic composite was investigated in strong concentration (1 molar) of methanol and ethanol, as it occurs at the cathode of an experimental direct alcohol fuel cell due to the alcohol crossover effect.

The Pt-ZrO_2/C electrocatalyst was evaluated in an experimental direct alcohol fuel cell where the data were recorded in an Electrochem fuel cell test station. The experiments were carried out at room temperature to assure the highest solubility of O_2 in the alcohol solution. Pt-Ru/C//nafion 115//Pt-ZrO_2/C constituted the mem-

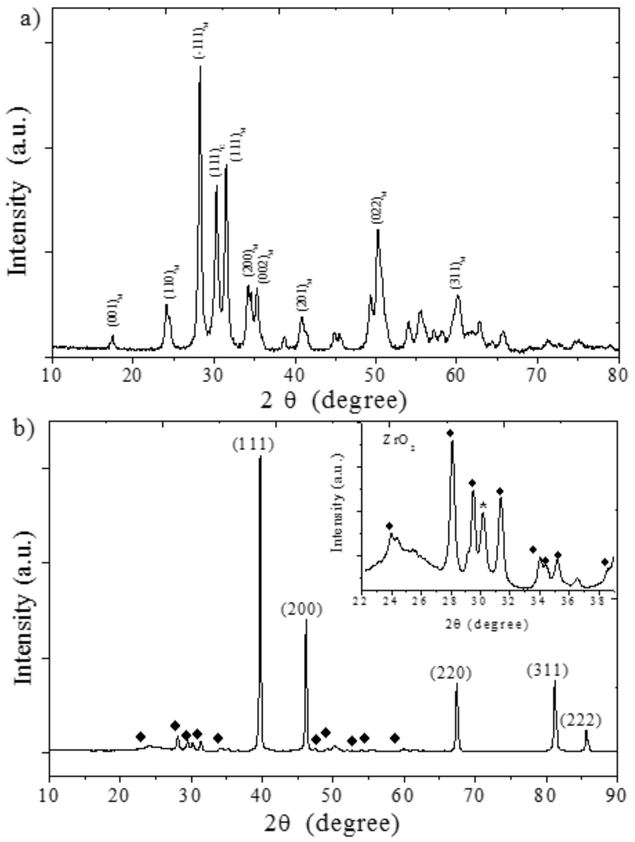

Figure 1. X-Ray diffraction patterns of samples: (a) ZrO$_2$ obtained by sol-gel, (b) Pt-ZrO$_2$/C electrocatalyst obtained by chemical reduction, (♦) monoclinic and (Ø) cubic structure.

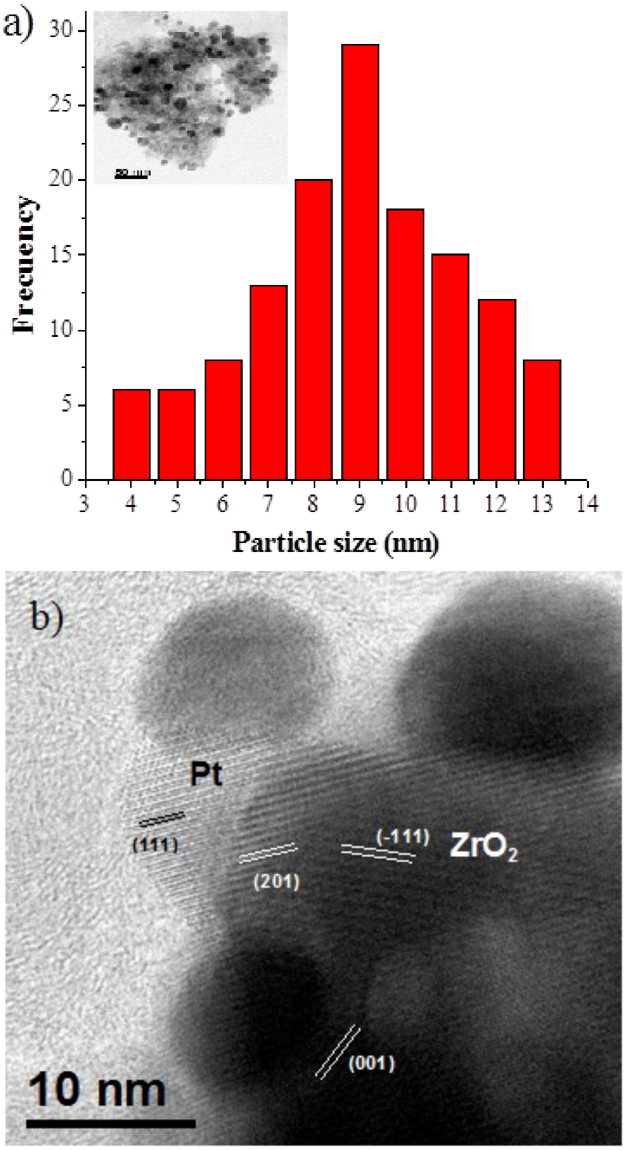

Figure 2. (a) Particle size distribution of Pt-ZrO$_2$/C , (b) TEM micrographs of the Pt-ZrO$_2$/C nanoparticles.

brane electrode assembly (MEA). Commercial Pt-Ru/C from E-Tek was used as the anodic electrocatalyst due to its stability for promoting the alcohol oxidation in this kind of fuel cells. The electrocatalytic loading of Pt-Ru/C in the anode was 0.4 mg·cm^2. Nafion membrane was activated prior to assemble it with the electrodes. The electrocatalytic loading of ZrO$_2$ in the cathode of the MEA was 0.4 mg·cm^2. The MEA tested in the DAFCs had 1 cm^2 of geometrical area. The oxygen flux in the cathode side of the fuel cell was 50 cm^3·min^{-1} and the fuel (methanol or ethanol) was fed in the anode side of the fuel cell at ca. 1 cm^3·min^{-1}. Reagent grade methanol and ethanol were used as received.

3. RESULTS AND DISCUSSION

3.1. Structural analysis of the Pt-ZrO$_2$/C composite

In Figure 1 are shown the XRD patterns of the ZrO$_2$ precursor (Fig. 1(a)) and the Pt-ZrO$_2$/C composite (Fig. 1(b)). Diffraction patterns of ZrO$_2$ (Fig. 1(a)) exhibit predominant peaks at 2q: 28.17°, 31.46° and 50.11° (JCPDS 37-1484), corresponding to (-111), (111) and (022) crystallographic planes of ZrO$_2$ monoclinic phase. It was also observed a unique peak corresponding to cubic phase of zirconia at 2q = 30.2° (JCPDS 49-1642), corresponding to the (111) plane. The formation of a predominant monoclinic phase was a result of the synthesis procedure used in this work to obtain ZrO$_2$. This structural characteristic can be adequate for the formation of ZrO$_2$ mesoporous powder. As a complementary analysis, the mesoporous characteristics of the ZrO$_2$ sample were studied by BET technique. Zirconia sample showed a monomodal pore size distribution in the range 17 to 29 nm, the porous volume was calculated as 0.104 cm^3·g^{-1} and the superficial area was calculated as 27.37 m^2·g^{-1}.

In Figure 1(b) are shown the XRD patterns for the Pt-ZrO$_2$/C electrocatalyst. It was possible to observe peaks of crystalline structures indicating the coexistence of Pt and ZrO$_2$ phases. The crystalline structure of Pt is *fcc*, with diffraction peaks appearing at 2q: 39°, 46°, 68°, 81° and 85°, corresponding to the planes (111), (200), (220), (311) and (222) respectively. The diffraction peaks found for ZrO$_2$ did not show any crucial change respect to the results discussed in Figure 1(a). It is clearly observed that from the synthesis of the electrocatalytic composite Pt was obtained very

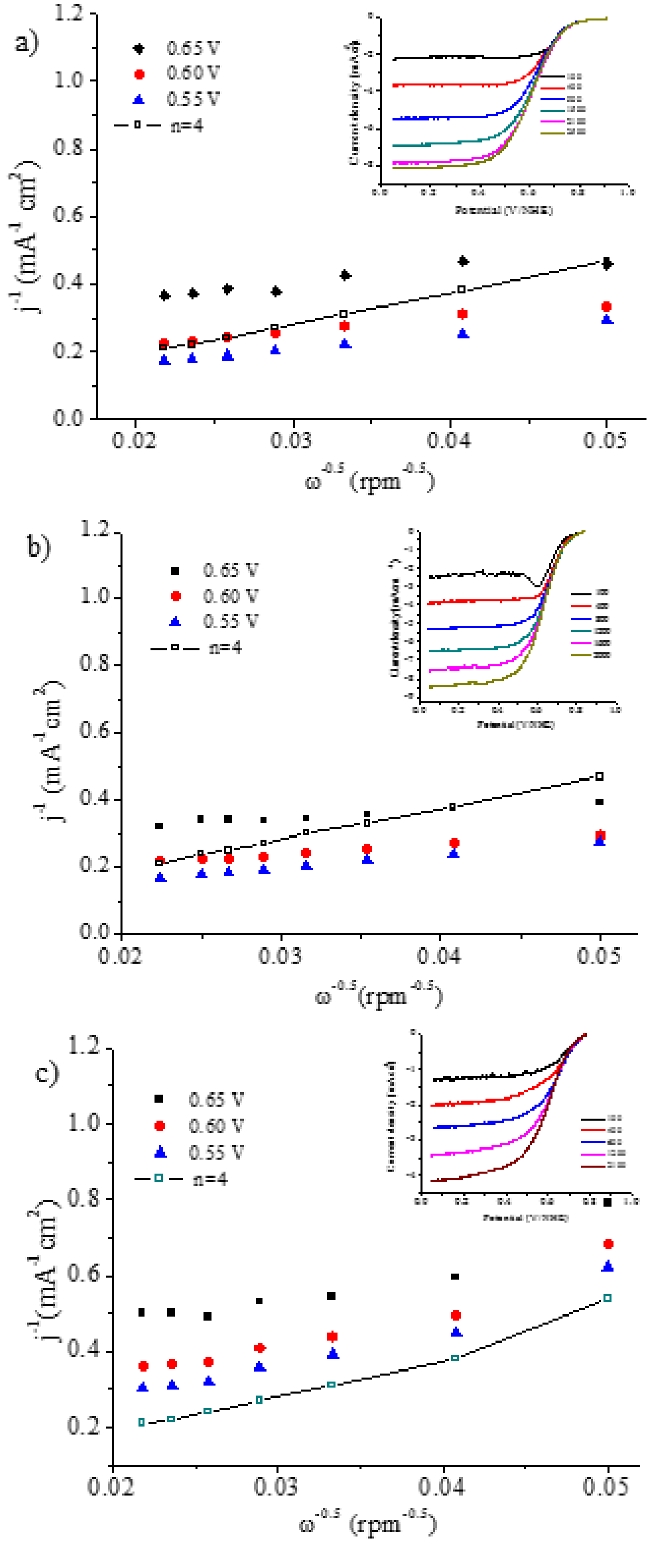

Figure 3. Koutecky-Levich plots at different potentials during the ORR on Pt-ZrO_2/C, (a) 0.5 M H_2SO_4 solution, (b) 0.5MH_2SO_4 + 1M CH_3OH , (c) 0.5MH_2SO_4 + 1M C_2H_5OH.

crystalline and ZrO_2 could be synthesized in a 2-D mesoparticulate array with a crystallite mean size of 4 nm according to the Scherrer formula for X-ray particle size determination.

3.2. Identification of Pt-ZrO_2/C composite nanoparticles by TEM

Figure 2 shows the micrographs of the Pt-ZrO_2/C electrocatalyst by transmission electron microscopy. In Figure 2(a) it is shown the image of the Pt-ZrO_2/C nanoparticles where it is observed the nanoparticles agglomeration of Pt and ZrO_2. At the low resolution image, it was possible to observe the interaction of quasi-spherical ZrO_2 nanoparticles forming a mesoporous continuum with the possibility to interact with the Pt nanoparticles embedded in the zirconia matrix. The electronic conductivity of the composite was assured by the presence of carbon surrounding it. A spherical Pt nanoparticle of 9 nm was anchored to a ZrO_2 nanoparticle of about 20 nm. Figure 2(b) shows a typical micrograph of the nanoparticles forming the composite. It was possible to consider that the coexistence of Pt-ZrO_2 phases and the mesoporous continuum could control the electrochemical response of this composite in the oxygen reduction reaction.

From the previous results, it was possible the synthesis of Pt nanoparticles (particle size less than 20 nm) anchored to the mesoporous zirconia.

3.3. Electrochemical characterization for oxygen reduction reaction in the presence of alcohol

Figure 3 shows the electrocatalytic activity of Pt-ZrO_2/C during the oxygen reduction reaction in acid medium in presence of methanol or ethanol as it could occur in an experimental condition by alcohol crossover from the anode to the cathode of the DAFC. The Koutecky-Levich plots were obtained by cyclic voltamperograms using a rotating disk electrode (RDE) and it was observed the oxygen reduction threshold at 0.90 V/NHE (Fig. 3(a)). In this case, the electrolyte was an O_2 saturated aqueous solution of 0.5M H_2SO_4. The oxygen reduction reaction threshold in aqueous solution with 1M methanol (Fig. 3(b)) and ethanol (Fig. 3(c)) was 0.84 and 0.78 V/NHE respectively. It means that the oxygen reduction reaction on Pt-ZrO_2/C is slightly affected by the strong concentration of alcohols in the O_2 saturated solution. Figure 3(b) and Figure 3(c) show that the oxygen reduction reaction on the surface of the composite electrocatalyst is carried out over 2000 rpm in the presence of methanol or ethanol respectively. It is possible to consider that the solubility of oxygen on methanol and ethanol in the proximity of the 2-D mesoparticulate array formed by the composite electrocatalyst could allow the reduction reaction without an apparent negative effect on the performance of the cathodic electrocatalyst as can be seen in these two figures. It is also possible that the presence of ZrO_2 interacting with the Pt nanoparticles could play an important role in the electrocatalytic activity during the oxygen reduction process by improving the tolerance to CO poisoning, solvation and the formation of parasitic intermediate species due to alcohol crossover (e.g. acetaldehyde or acetic acid).

Tafel analysis was performed to identify the electro-kinetic characteristics of the oxygen reduction reaction on Pt-ZrO_2/C in strong alcohol environments. Figure 4 shows the Tafel plots corresponding to the kinetic response of ORR on Pt-ZrO_2/C in three aqueous media: 0.5M H_2SO_4, 0.5M H_2SO_4 + 1M CH_3OH, 0.5M H_2SO_4 +

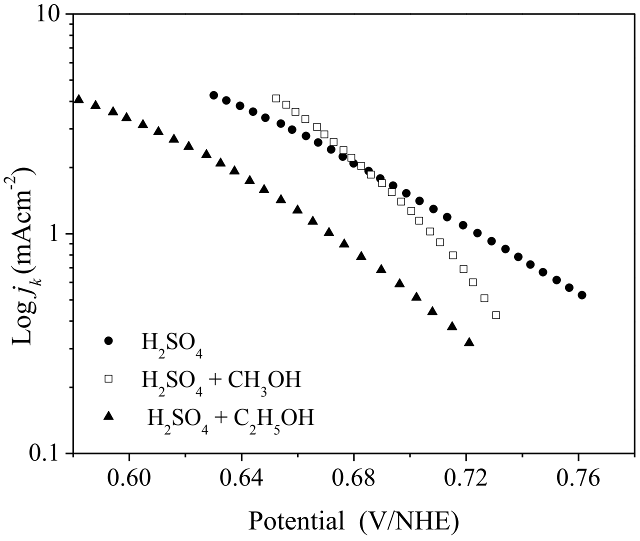

Figure 4. Tafel plots for the ORR on Pt-ZrO$_2$/C electrocatalytic composite in O.5M H_2SO_4

1M C_2H_5OH. The reaction mechanism for the ORR in the three media involves the transfer of 4 electrons as usually occurs in hydrogen-oxygen fuel cells (Table 1). In Figure 4 it is observed the changes in kinetic current density due to the presence of strong methanol or ethanol solutions. The presence of alcohol in the cathode of a DAFC modifies the onset potential of the ORR taking along to lower potential values, affecting the voltage of the fuel cell and this effect is more significant in the case of ethanol environment as can be seen in Figure 4. Table 1 shows the electrocatalytic parameters calculated from Tafel plots and it is possible to associate the presence of alcohol to the loss of electrochemical effective area (A_{ECE}) of the cathodic electrocatalyst. In the case of methanol interacting with the ORR, the original effective area of the Pt-ZrO$_2$/C diminished 17%, and when ethanol interacted in the reduction reaction, A_{ECE} was reduced by 58%. Nevertheless, the complementary kinetic parameters as Tafel slope, exchange current density and charge transfer coefficient indicate that the oxygen reduction reaction is performed in three media (H_2SO_4, H_2SO_4+CH_3OH, H_2SO_4+C_2H_5OH) with no substantial changes in the kinetic values. The electrochemical analysis has proved that Pt-ZrO$_2$/C has the capability to reduce oxygen still under extreme conditions of alcohol crossover.

Table 1. Kinetic values of the oxygen reduction reaction on Pt-ZrO$_2$/C based electrocatalyst.

Electrolyte	*E* (V/NHE)	*-b* (mV/Dec)	j_o mA×cm^{-2}	α	*n*	A_{ECE} cm^2
H_2SO_4	0.9	134	1.78*10^{-4}	0.44	4	2.9
H_2SO_4+ CH_3OH	0.84	121	6.35*10^{-5}	0.48	4	2.4
H_2SO_4+ C_2H_5OH	0.78	130	5.11*10^{-5}	0.45	4	1.2

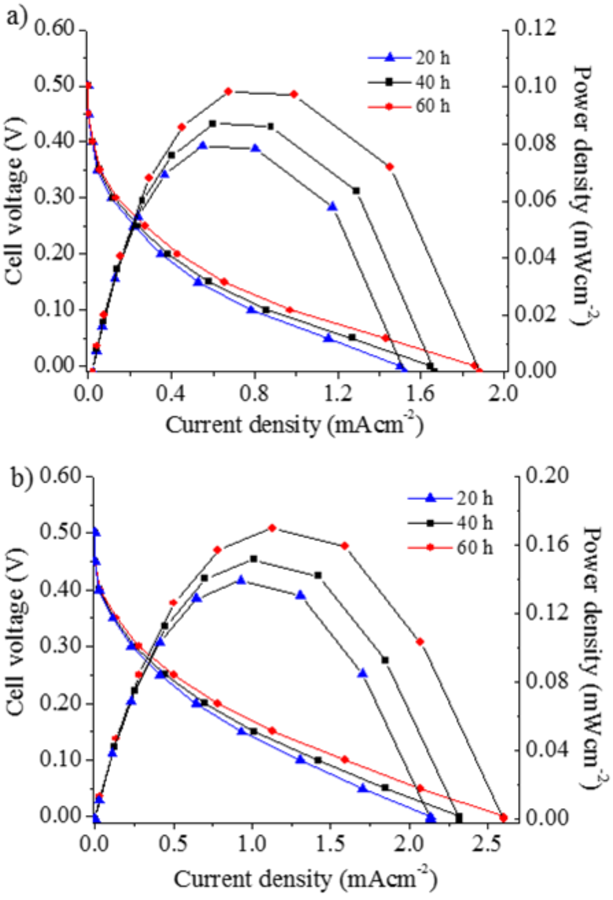

Figure 5. Performance curves of DAFC single cell with Pt-Ru/C anode catalyst and Pt-ZrO$_2$/ cathode catalyst, (a) in presence of 1M methanol , (b) 1M ethanol.

In Figure 5 are shown the I-V characteristics of the direct alcohol fuel cells supplied with methanol or ethanol. All the experiments were carried out at room temperature, the alcohol concentration was 1 mol·L^{-1} at a flow rate of 1cc·min^{-1} and oxygen was supplied at a flow rate of 50 cc·min^{-1}. Commercial Pt-Ru/C was used as the anode electrocatalyst to oxide alcohol and Pt-ZrO$_2$/C synthesized in this works was used as cathodic electrocatalyst to carry out the oxygen reduction reaction in the experimental fuel cell. The DAFCs were operating for 60 hours in continuous performance.

In Figure 5(a) it is shown the I-V performance of the direct alcohol fuel cell supplied with methanol/oxygen and operating for 20, 40 and 60 h. From the start up to 60 h, there was an increase of ca. 24% in the power density of the cell. The cell voltage was maintained constant at 0.5 V and the increase was observed in the current density from 1.55 to 1.9 mA·cm^{-2}, obtaining for DAFC, a maximum power density of ca. 10 mW·cm^{-2}. The improvement in the electric power of the DAFC supplied with methanol, as a function of time, could be correlated to the methanol crossover tolerance properties of Pt-ZrO$_2$/C in the cathode, allowing the performing of the redox reaction at the fuel cell.

Pt-ZrO$_2$/C was also evaluated in a DAFC supplied with ethanol/oxygen up to 60 hours at room temperature (Figure 5(b)). The power density of the cell increased ca. 22% in that period. The cell voltage was maintained constant at 0.5 V and the variation was observed in the current density of the fuel cell from 2.13 to 2.60 $mA\cdot cm^{-2}$. The I-V values obtained in this experiment showed the capability of Pt-ZrO_2/C for reducing oxygen in the experimental direct alcohol fuel cell for 60 h where the ethanol crossover could not cause significant effects on the cathode side of the fuel cell.

The results shown in Figure 5 indicate the positive effect of using monoclinic zirconia on the electrocatalytic properties of Pt as the main electrocatalyst for improving the reduction reaction in a DAFC. The Pt-ZrO_2/C based composite provided active sites for the adsorption of O_2 molecules and this process improved the oxygen electro-reduction and the tolerance to alcohol crossover to the cathode of the fuel cell. It is possible to consider that the active surface of Pt-ZrO_2/C is inside the interconnected 2-D array where the alcohol is not easy to reach. This effect could be improved by the solubility of oxygen in the methanol and ethanol solution at room temperature with the possibility to lead oxygen molecules to the active sites.

4. CONCLUSIONS

The nanostructured composite based on Pt-ZrO_2/C at 10 wt.% and synthesized by two-step chemical reduction showed adequate characteristics for performing the oxygen reduction reaction on the cathode of direct alcohol fuel cells fed with methanol and ethanol. The reaction mechanism analysis revealed transfer of four electrons in both fuel cells for carrying out the ORR at room temperature, inclusively in the case of strong presence of alcohol in the cathode of the fuel cell considering the alcohol crossover as a consequence of a long time fuel cell performance. The direct ethanol and direct methanol fuel cells showed stable conditions during 60 hours of performance directly related to the use of electrocatalytic composites in the cathode of the fuel cells. It was observed that the incorporation of a monoclinic structure of ZrO_2 improved the electrocatalytic properties of the Pt for promoting the oxygen reduction reaction at room temperature still in presence of strong alcohols.

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