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Preparation of PtRu/C Electrocatalysts Using Citric Acid as Reducing Agent and OH- ions as Stabilizing Agent for Direct Alcohol Fuel Cell (DAFC)

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PtRu/C electrocatalysts (Pt:Ru atomic ratio of 50:50 and 80:20) were prepared using citric acid as reducing agent and OH^- ions as stabilizing agent. The obtained electrocatalysts were characterized by energy dispersive X-ray analysis and transmission electron microscopy. The electro-oxidation of methanol and ethanol were studied at room temperature by chronoamperometry. Studies on the Direct Methanol Fuel Cell (DMFC) and Direct Ethanol Fuel Cell (DEFC) were carried at 90°C. For both electrocatalysts the obtained Pt:Ru atomic ratios were similar to the nominal ones and the average particles sizes were around 2.5 nm. The chronoamperometry and DAFC experiments showed that the electrocatalyst prepared with Pt:Ru atomic ratio of 80:20 has a superior performance for methanol oxidation, while the electrocatalyst prepared with Pt:Ru atomic ratio of 50:50 has a superior performance for ethanol oxidation.

Keywords: PtRu/C, methanol oxidation, citric acid, ethanol oxidation, fuel cell

1. INTRODUCTION

Fuel cells employing alcohols directly as combustible (Direct Alcohol Fuel Cell, DAFC) are attractive as power sources for mobile, stationary and portable applications. Compared to hydrogen-fed fuel cells, which need a reforming system or have problems of hydrogen storage, DAFCs use a liquid fuel, thus simplifying the fuel delivery system [1–6]. Methanol has been considered the most promising fuel, because it is more efficiently oxidized than other alcohols. However, slow anode kinetics was observed and the methanol crossover through the membrane also decreases the efficiency [7–9]. As an alternative to methanol, ethanol could be produced in large quantities from biomass and it is much less toxic than methanol. However, its complete oxidation to CO_2 is more difficult than that of methanol due to the difficulties in C–C bond breaking and the formation of CO intermediates that poison the platinum anode catalysts [10–12]. Carbon-supported platinum is commonly used as anode catalyst in low-temperature fuel cells; however, pure Pt is not an efficient anodic catalyst for the direct alcohol fuel cells, because it is rapidly poisoned by strongly adsorbed species coming from the dissociative adsorption of methanol or ethanol. Due to the low activity of platinum for practical DAFC applications, elements like ruthenium have been added to promote electroactivity [12]. Studies have been shown that the catalytic activity of PtRu/C electrocatalysts is strongly dependent on the method of preparation. Thus, new preparation methods of PtRu/C electrocatalyts have been one of the major topics studied on the electro-oxidation of alcohols [13]. Citric acid and sodium citrate have been used as stabilizing agent in the preparation of electrocatalysts. Guo *et al.* [14] prepared a well-dispersed Pt/C electrocatalyst by the reduction of chloroplatinic acid with sodium borohydride, with citric acid as a stabilizing agent in ammonium hydroxide solution. The results indicate that the oxygen reduction reaction activity of the obtained catalyst was comparable to that of commercial Pt/C catalyst. Lin *et al* [15] prepared platinum nanoparticles of 2–3 nm average size by methanol reduction using sodium citrate as the stabilizer. Shimazaki *et al* [16] prepared PtRu nanoparticles in aqueous media using citric acid as a capping agent and $NaBH_4$ as a reducing agent with the aid of pH control. The average size of the PtRu nanoparticles was ca. 2 nm and the electrochemical measurement showed that the PtRu nanoparticles had catalytic activity for methanol. Guo *et al.* [17] prepared PtRu/C nanocatalysts by changing the molar ratio of citric acid to platinum and ruthenium metal salts and using sodium borohydride as a reducing agent. The obtained materials were tested as anode of a direct methanol fuel cell (DMFC) and showed a slightly higher performance than the commercial catalyst.

In this work, PtRu/C electrocatalyts were prepared using citric acid (CA) as reducing agent and OH^- ions as stabilizing agent. The obtained materials were tested for methanol and ethanol oxidation.

2. EXPERIMENTAL PART

PtRu/C electrocatalysts (20 wt% of metal loading) were prepared in a single step using. $H_2PtCl_6.6H_2O$ (Aldrich) and $RuCl_3{\cdot}x$H2O (Aldrich) as metals sources and Vulcan XC72R as carbon support. The metal sources, the citric acid (CA:PtRu molar ratio of 1:1) and a solution of KOH 1 mol L^{-1} (OH^-:PtRu molar ratio of 10:1) were dissolved in water and the carbon support was added. The resulting mixtures was treated in an ultrasound bath for 5 min and submitted to reflux for 3 h under open atmosphere. Finally, the mixtures were filtered and the obtained solids were washed with water and dried at 70◦C for 2 h.

The Pt:Ru atomic ratios were obtained by EDAX analysis using a scanning electron microscope Philips XL 30 with a 20KeV electron beam and equipped with EDAX DX-4 microanaliser.

Transmission electron microscopy (TEM) was carried out using a Carl Zeiss CEM 902 apparatus with a Proscan high-speed slow-scan CCD camera and digitalized (1024×1024 pixels, 8 bits) using the Analysis software. The particle size distributions were determined by measuring the nanoparticles from micrographs using Image Tool Software.

Chronoamperometry experiments were performed at 25 ^{0}C with 1.0 mol L^{-1} of methanol or ethanol in 0.5 mol L^{-1} H_2SO_4 solutions saturated with N_2 using a Microquimica (model MQPG01, Brazil) potenciostat/ galvanostat. [18].

The membrane electrode assemblies (MEA) were prepared by hot pressing a pretreated Nafion 117 membrane placed between either a PtRu/C (50:50), PtRu/C (80:20) prepared by citric acid or PtRu/C (50:50) E-tek anode (1 mg Pt cm^{-2} catalyst loading) and a 20 wt% Pt/C E-TEK cathode (1 mg Pt cm^{-2} catalyst loading) at 125 ^{0}C for 2 min under a pressure of 225 kgf cm^{-2}. The direct methanol or ethanol fuel cell performances were determined in a single cell with an area of 5 cm^2. The temperature was set to 90 ^{0}C for the fuel cell and 80 ^{0}C for the oxygen humidifier. The fuel was 2 mol L^{-1} of methanol or ethanol solution delivered at approximately 2 mL min^{-1} and the oxygen flow was regulated at 500 mL min^{-1} and pressure of 2 bar. Polarization curves were obtained by using a TDI RBL 488 electronic load.

3. RESULTS AND DISCUSSION

In a previous work [19] the effect of CA:PtRu molar ratio in the preparation of PtRu/C electrocatalyts using citric acid as reducing agent was studied (CA:PtRu molar ratio of 1:1, 1:5 and 1:10). The obtained materials showed an average nanoparticle size of approximately 10 nm and similar activities for methanol oxidation. The great size of the PtRu nanoparticles obtained in preparation of PtRu/C electrocatalysts using citric acid as reducing agent was also observed by Pillai and Kamat [20] in the preparation of Ag nanoparticles using citrate as reducing agent. They attributed the nanoparticles growth to the complexation of citrate ions by silver seeds as soon as they were formed in the initial reduction step. In this manner, citrate ions were removed from the bulk solution resulting in relatively fewer new seeds of silver. Thus, with fewer initial silver seeds, the Ag^+ ions were reduced at the silver clusters surface and a growth of the nanocrystals was observed. In this work, we studied the addition of OH^- ions to the reaction medium with the aim to decrease of the crystallite sizes of the PtRu/C electrocatalysts prepared using citric acid as reducing agent (Table 1). In the preparation of the electrocatalysts the OH^- ions could be adsorbed on the PtRu nanoparticles surface inhibiting their growth [21].

Table 1. Pt:Ru atomic ratios and mean particle sizes of the PtRu/C electrocatalysts prepared using citric acid as reducing agent (20 wt% metal loading, CA:PtRu molar ratio of 1:1 and OH^-:PtRu molar ratio of 10:1)

Pt:Ru atomic ratio - nominal	Pt:Ru atomic ratio - EDX	Average particle size (nm)
50:50	48:52	2.6
80:20	78:22	2.2

For both prepared PtRu/C electrocatalysts the obtained Pt:Ru atomic ratios determined by EDX analysis were similar to the nominal ones. The average particle sizes for both catalysts were around 2.5 nm (Table 1 and Fig. 1).

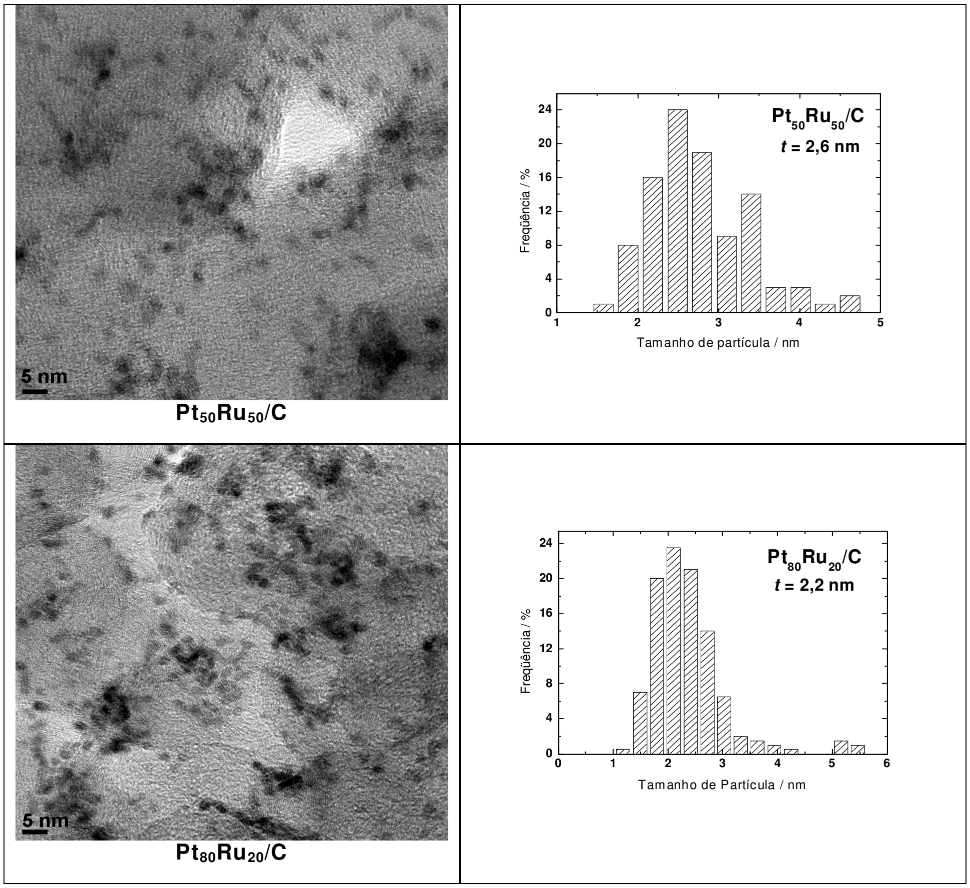
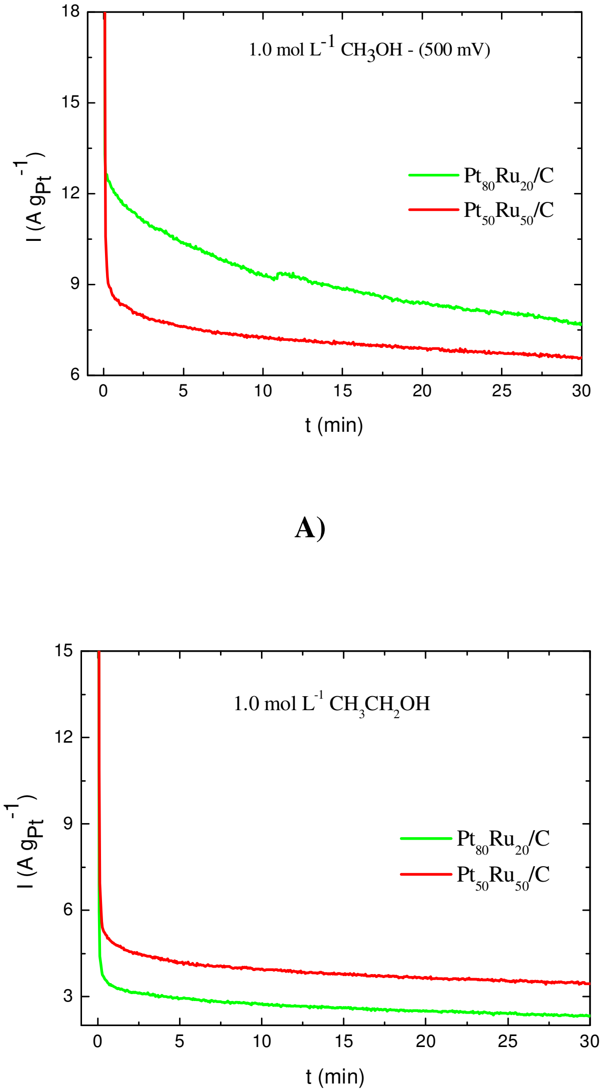


Figure 1. TEM micrographs and histograms of PtRu/C electrocatalysts

Compared to the PtRu/C electrocatalysts prepared without addition of OH^- ions into the reaction medium [19], which have average particles size of around 10 nm, a great decrease of the sizes of the obtained nanoparticles and a good distribution on the carbon support were observed.

The PtRu/C eletrocatalysts performances for methanol and ethanol oxidation were studied by chronoamperometry in 1.0 mol L^{-1} of alcohol in 0.5 mol L^{-1} H_2SO_4 at an anodic potential of 0.5V versus RHE (Fig. 2 A and B).

The current values were normalized per gram of platinum, considering that methanol adsorption and dehydrogenation occur only on platinum sites at room temperature [22]. For methanol electro-oxidation (Fig 2A) PtRu/C electrocatalyt with Pt:Ru atomic ratio of 80:20 showed a superior performance compared to the electrocatalyst prepared with Pt:Ru atomic ratio of 50:50. On the other hand, for ethanol-oxidation (Fig. 2B) the eletrocatalyst prepared with Pt:Ru atomic ratio of 50:50 showed a superior performance. Similar results were observed using PtRu/C prepared by spontaneous deposition of platinum on carbon-supported ruthenium nanoparticles [23], where for methanol oxidation good performance was observed with high platinum coverage and for ethanol oxidation with low platinum coverage. The best performance of PtRu/C electrocatalyt with Pt:Ru atomic ratio of 80:20 could be explained based on the number of Pt atoms necessary to activate the adsorption of methanol (three to five) and the number of ruthenium atoms to activate water (one atom usually) [23-25], while for ethanol electro-oxidation it has been observed that its increase with more ruthenium content [11, 26].

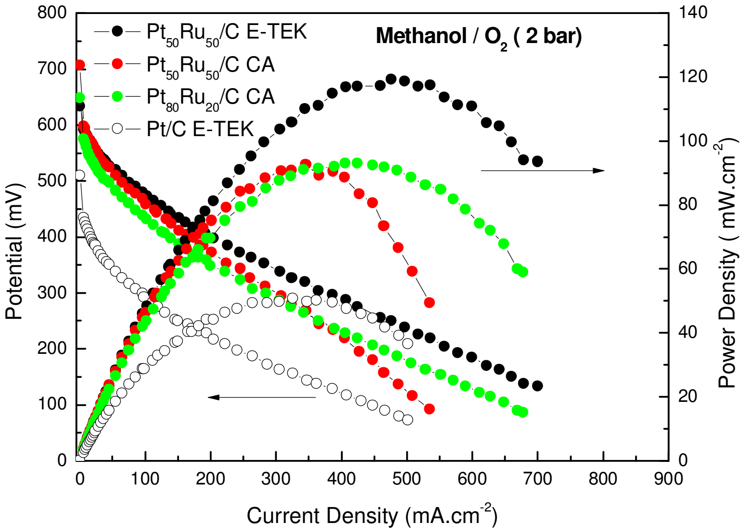


A)

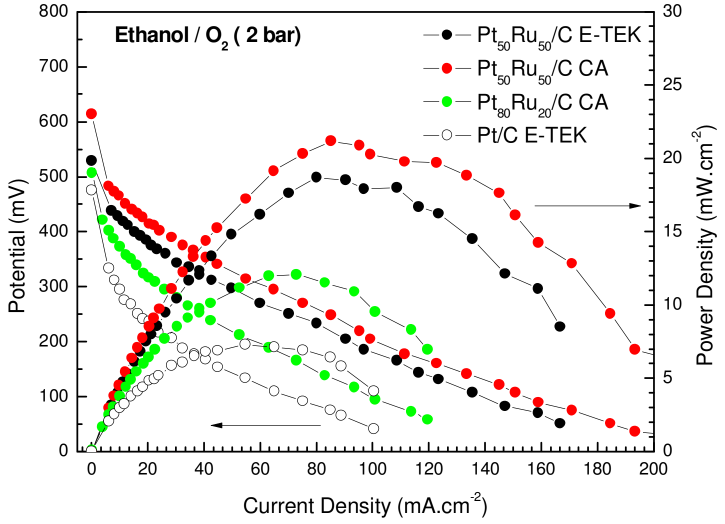
B)

Figure 2. Current–time curves at 0.5 V in 0.5 mol L^{-1} H_2SO_4 containing 1.0 mol L^{-1} of **A)** methanol and **B)** ethanol for PRu/C electrocatalysts.

Figure 3 show the performances of direct methanol (DMFC) or direct ethanol fuel cell (DEFC) using PtRu/C electrocatalysts prepared using CA and commercial Pt/C and PtRu/C from E-TEK as anodes. In both cases, all PtRu/C electrocatalysts were more active than Pt/C E-TEK for DMFC and DEFC studies, which could be attributed to the bifunctional mechanism [23]. For DMFC the maximum power density of commercial PRu/C E-TEK electrocatalyst (120 mW cm^{-2}) was greater than that of PtRu/C (50:50) and PtRu/C (80:20) electrocatalyst (90mWcm^{-2}), while for DEFC studies PtRu/C (50:50) (22 mW cm^{-2}) prepared using CA was more active than PtRu/C E-TEK (17 mW cm^{-2}) and PtRu/C (80:20) prepared using CA (11 mW cm^{-2}).



A)



B)

Figure 3. Electrical performances of a 5 cm^2 **A)** DMFC and **B)** at 90 ^{0}C using PtRu/C electrocatalysts (CA) and commercial Pt/C and PtRu/C (50:50) from E-TEK anodes (1 mg Pt cm^{-2} catalyst loading) and Pt/C E-TEK cathode (1 mg Pt cm^{-2} catalyst loading), Nafion 117 membrane, alcohol (2.0 mol L^{-1}), oxygen pressure (2 bar).

4. CONCLUSIONS

Active PtRu/C electrocatalysts for methanol and ethanol oxidation could be prepared using citric acid (CA) as reducing agent and OH^- ions as stabilizing agent. The addition OH^- ions leads to a decrease of the average nanoparticles sizes. The Pt:Ru atomic ratio has an important effect on the catalytic activity of the prepared PtRu/C electrocatalysts for methanol and ethanol oxidation.

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