

Short communication

# Electro-oxidation of ethanol on PtRu/C electrocatalysts prepared from $(\eta\text{-C}_2\text{H}_4)(\text{Cl})\text{Pt}(\mu\text{Cl})_2\text{Ru}(\text{Cl})(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})$

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## Abstract

PtRu/C electrocatalysts were prepared by impregnation of the complex  $(\eta\text{-C}_2\text{H}_4)(\text{Cl})\text{Pt}(\mu\text{Cl})_2\text{Ru}(\text{Cl})(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})$  on to a carbon support. The complex/support was subjected to different thermal treatments and tested for ethanol electro-oxidation using the thin porous coating electrode technique. The electrocatalysts were characterized by transmission electron microscopy (TEM), EDAX and cyclic voltammetry. The electrocatalyst treated under hydrogen flow and subjected to an oxidative thermal treatment had a superior performance to that of a commercial catalyst, which could be attributed to the better control of the metallic platinum and oxidized ruthenium species on the PtRu nanoparticle surface.

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## 1. Introduction

PtRu/C electrocatalysts have superior activity as an anode in direct methanol fuel cells (DMFC) and CO-tolerant proton-exchange membrane fuel cells (PEMFC) [1,2]. Some studies have shown that the best performance was obtained using a Pt:Ru atomic ratio of 1:1 [3,4]. However, the conventional methods of preparation of bimetallic supported nanoparticles like wet impregnation of metal salts and chemical reduction in hydrogen atmosphere seem not to provide satisfactory control of the particle size, distribution and composition. Shapley and co-workers [5,6] reported the synthesis and characterization of carbon-supported PtRu nanoparticles using the neutral complexes  $\text{PtRu}_5\text{C}(\text{CO})_{16}$  and  $\text{Pt}_2\text{Ru}_4(\text{CO})_{18}$  as a single molecular precursor. The structural characterization of the bimetallic nanoparticles revealed Pt:Ru compositions of 1:5 and 2:4, respectively, and an average diameter between 1.0 and 1.5 nm. Based on these results, Lukehart and co-workers [7] prepared a PtRu/C electrocatalyst using the complex  $(\eta\text{-C}_2\text{H}_4)(\text{Cl})\text{Pt}(\mu\text{Cl})_2\text{Ru}(\text{Cl})(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})$  as a 1:1 Pt:Ru bimetallic molecular precursor and Vulcan XC72R as the traditional carbon powder support. The precursor/carbon was ther-

mally treated under appropriate oxidizing and reducing conditions. XRD and on-particle EDS analyses revealed that the PtRu nanoparticles have a nearly 1:1 metal alloy stoichiometry. The measurements of the catalytic activity as an anode catalyst in DMFC revealed that the 50 wt.% PtRu catalyst showed a superior performance to that of a 60 wt.% PtRu commercial catalyst (E-TEK). Further studies also show that the performance of the catalyst could be enhanced using other carbon compounds as a support [8,9].

Ethanol is a renewable and attractive fuel for direct alcohol fuel cell (DAFC) as it is much less toxic than methanol and can be produced in great quantities from biomass. In Brazil, ethanol has been produced, distributed and used as a fuel for internal combustion engine cars for more than 20 years. Wang et al. [10] tested ethanol as a fuel using a PtRu electrocatalyst as anode and a phosphoric acid doped polybenzimidazole membrane at 170 °C. They observed that under these conditions the behavior of ethanol was close to that methanol. Lamy et al. [11] tested different binary electrocatalysts in the direct oxidation of ethanol and among them PtRu and PtSn were the most active and the least poisoned.

In this work, the PtRu/C electrocatalysts, prepared using the complex  $(\eta\text{-C}_2\text{H}_4)(\text{Cl})\text{Pt}(\mu\text{Cl})_2\text{Ru}(\text{Cl})(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})$  as a single-source molecular precursor, were submitted to different thermal treatments and tested for ethanol oxidation using the thin porous coating electrode technique.

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## 2. Experimental

The complex  $(\eta\text{-C}_2\text{H}_4)(\text{Cl})\text{Pt}(\mu\text{Cl})_2\text{Ru}(\text{Cl})(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})$  was synthesized and characterized as described by Lukehart and co-workers [7,9]. The PtRu/C electrocatalysts (20 wt.%, Pt:Ru atomic ratio of 1:1) were prepared in the following manner. The required quantity of complex was dissolved in a small quantity of dichloromethane and to this solution was added the appropriate mass of carbon support (Vul-

can XC72R). The resulting slurry was stirred for 30 min under argon and after this the solvent was removed at reduced pressure. The black solid obtained was submitted to different thermal treatments in a tube furnace with controlled atmosphere. The samples treated under hydrogen atmosphere were heated from room temperature to 400 or 650 °C at 1 °C min<sup>-1</sup> under argon flow. When the activation temperature was reached, hydrogen gas was introduced and the catalyst was held at that temperature for 2 h. Finally,

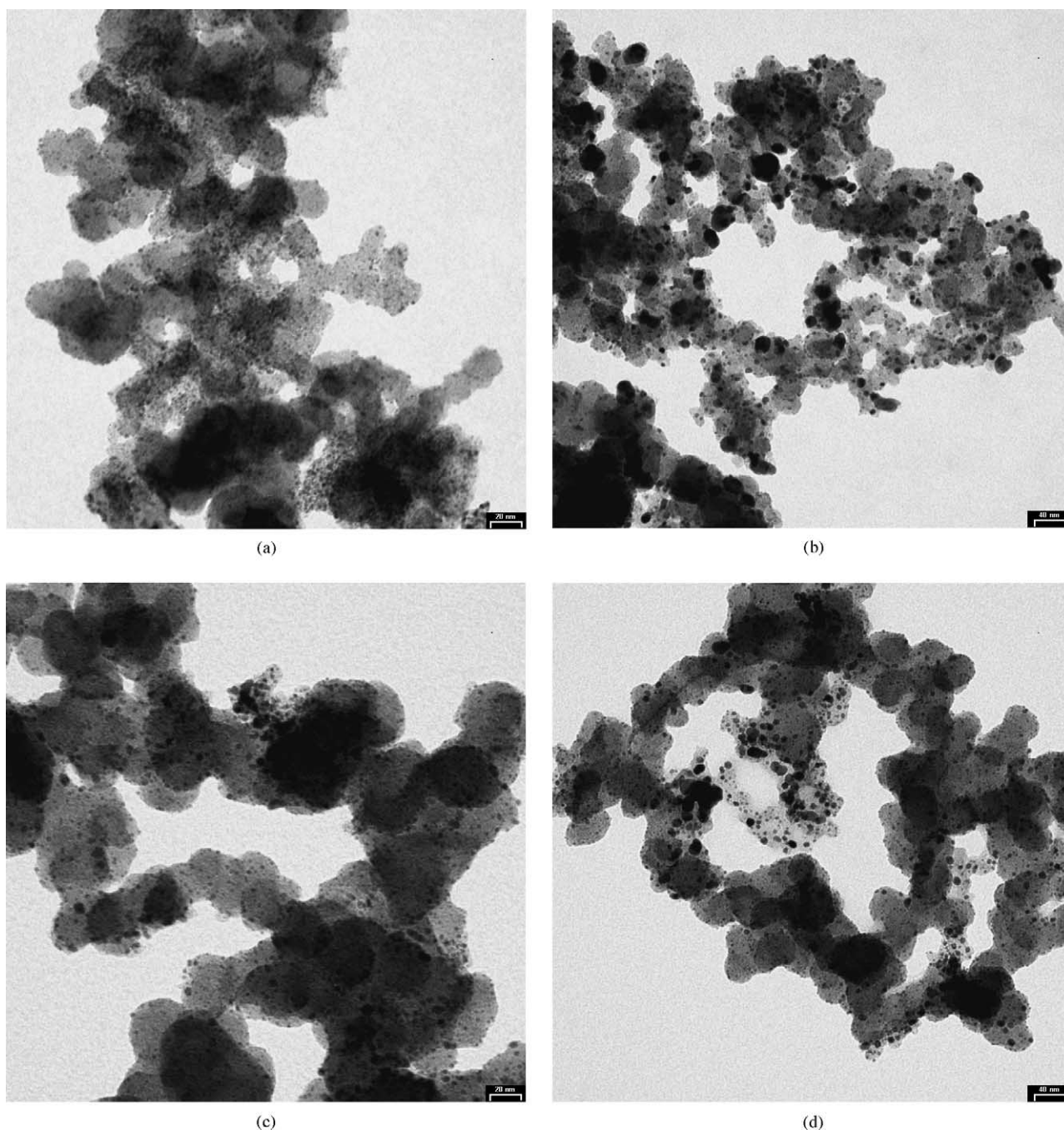


Fig. 1. TEM micrographs of the electrocatalysts: (a) treated at 400 °C under argon flow; (b) treated at 650 °C under argon flow; (c) treated at 400 °C under hydrogen flow; (d) treated at 650 °C under hydrogen flow; (e) treated at 400 °C under hydrogen flow and submitted to the oxidative thermal treatment; (f) treated at 650 °C under argon flow and submitted to the oxidative thermal treatment.

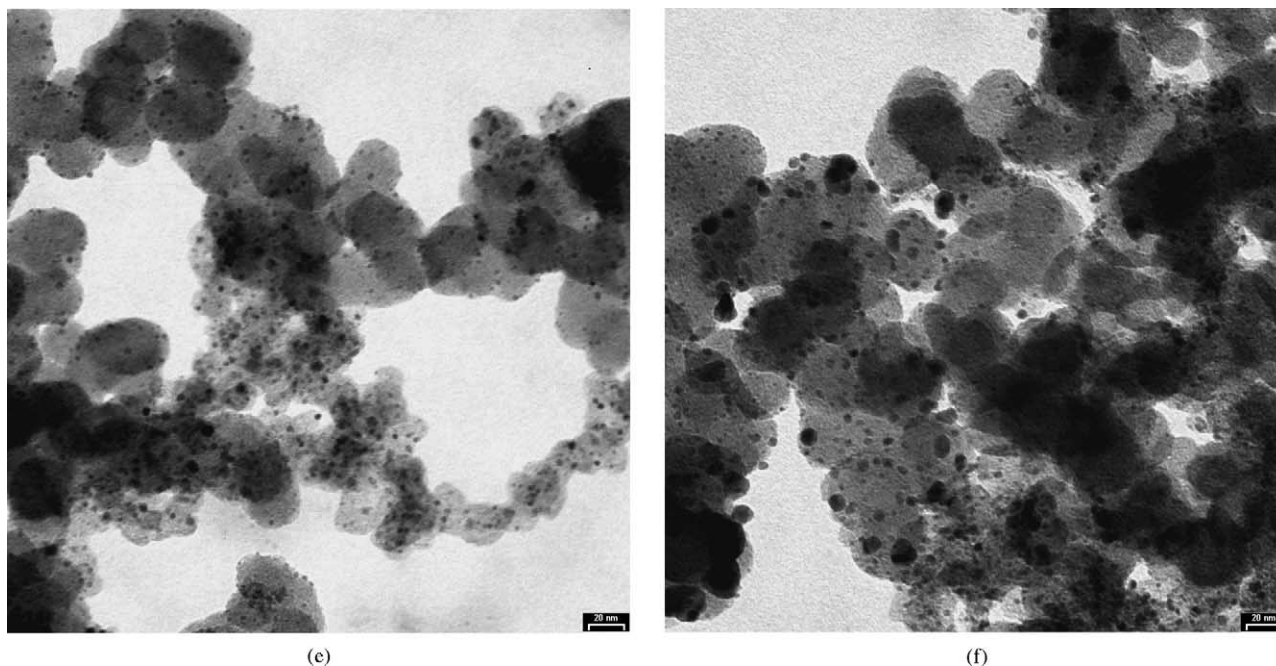


Fig. 1. (Continued).

the sample was cooled to ambient temperature under argon flow. The samples treated under argon were submitted to the same treatment under argon atmosphere all the time. The samples treated under hydrogen at 400 °C and treated under argon at 650 °C were also submitted to a further treatment: the samples were heated from room temperature to 300 °C at 5 °C min<sup>-1</sup> under air atmosphere for 30 min.

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.

The Pt:Ru atomic ratios were obtained by EDAX analysis using a scanning electron microscope Philips XL30 with a 20 keV electron beam and using a EDAX DX-4 microanalyzer.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique. The working electrode was constructed using a PTFE cylinder with a cavity 0.15 mm deep and 0.36 cm<sup>2</sup> area. A known amount of the electrocatalyst was treated with a 2% PTFE suspension and transferred quantitatively to the cavity. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Electrochemical measurements (cyclic voltammetry) were made using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer and using Microquimica software. Cyclic voltammetry was performed in a 0.5 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution saturated with N<sub>2</sub>. The evaluation of ethanol oxidation was performed at 25 °C in three different concentrations of ethanol: 0.1, 0.5 and 1.0 mol l<sup>-1</sup>. For comparative purposes,

a commercial carbon-supported PtRu catalyst from E-TEK<sup>®</sup> (20 wt.%, Pt:Ru molar ratio 1:1, lot # 3028401) was used.

### 3. Results and discussion

The electrocatalysts were prepared by the impregnation of the PtRu complex on to the carbon support and the resulting solids were submitted to different thermal treatments. The TEM micrographs of the electrocatalysts are shown in Fig. 1. In a general manner, the electrocatalysts treated at 400 °C (Fig. 1a, c and e) show the metal particles dispersed on the carbon support having an average particle size of 2.5 ± 1.0 nm, while the electrocatalysts treated at 650 °C (Fig. 1b, d and f) have a broader size distributions with an average particle size of 5.0 ± 3.0 nm. The broad area EDAX analysis of the electrocatalysts (Fig. 1a–f), on the micrometer scale, showed the emission lines from Pt and Ru with relative intensities corresponding to Pt:Ru atomic ratios between 1.0 and 1.3. Lukehart and co-workers [7,9] described similar particles size distributions and Pt:Ru atomic ratios on the micrometer scale. The on-particle EDS analysis also revealed Pt:Ru atomic ratios of approximately 1:1 [7].

The results of cyclic voltammetry experiments, in the absence of ethanol, are shown in Fig. 2. The electrocatalysts do not have a well-defined hydrogen oxidation region, as observed for pure platinum, and the currents in the double layer are larger. These results are characteristic of electrocatalysts with Pt:Ru atomic ratio of 1:1 [12,13]. However, some differences are apparent among the electrocatalysts. The electrocatalysts treated under hydrogen flow (Fig. 2a) and E-TEK have a more characteristic hydrogen region (0.05–0.40 V),

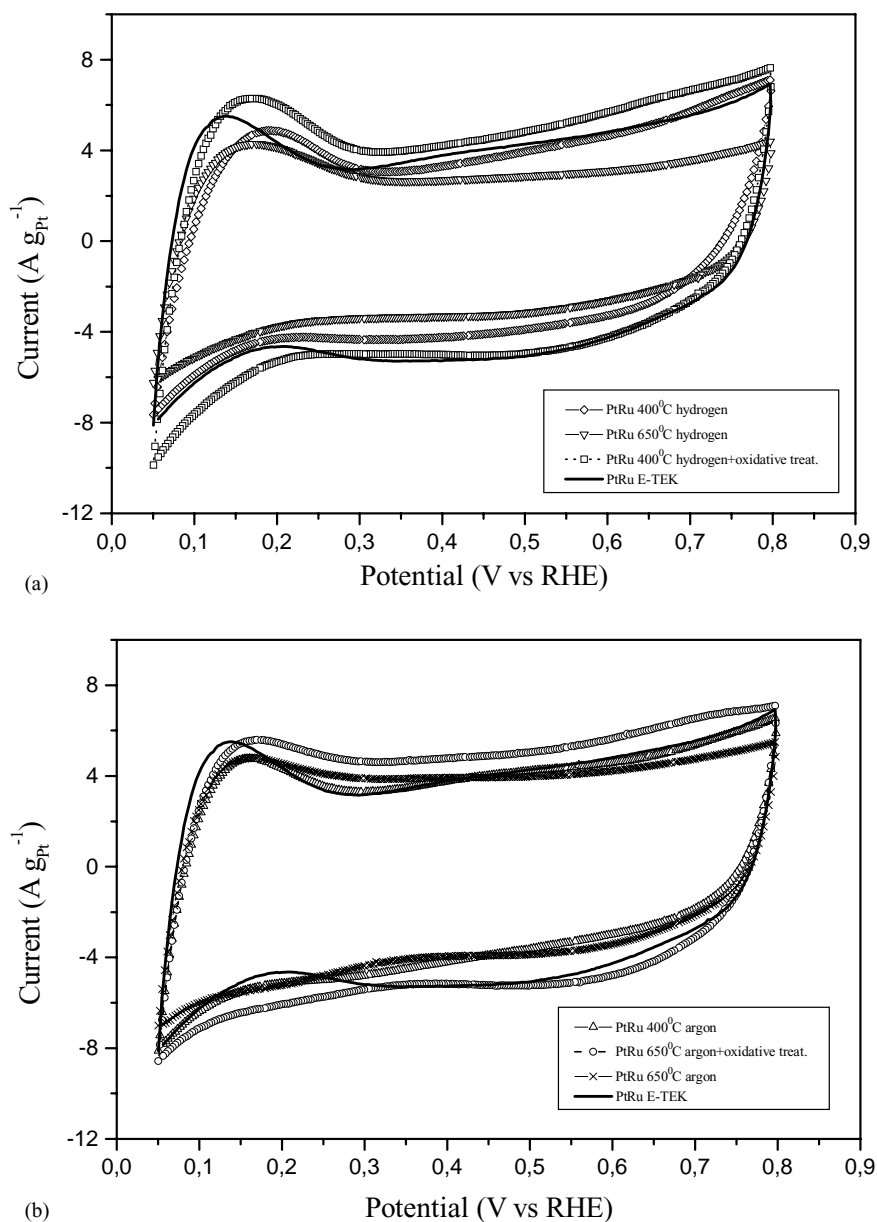


Fig. 2. Cyclic voltammety of the electrocatalysts in  $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$  with a sweep rate of  $10 \text{ mV s}^{-1}$ : (a) treated under hydrogen flow; (b) treated under argon flow.

while the electrocatalysts treated under argon flow (Fig. 2b) show a less defined peak in the hydrogen region. The electrocatalysts submitted to the oxidative thermal treatment have the larger currents in the double layer region. The electrocatalyst treated at  $400^\circ\text{C}$  under hydrogen flow and submitted to the oxidative thermal treatment (Fig. 2a) has the more defined hydrogen region and the larger currents in the double layer region.

The electro-oxidation of ethanol was studied varying the concentration from  $0.1$  to  $1.0 \text{ mol l}^{-1}$  (Fig. 3). In the hydrogen region ( $0$ – $0.4 \text{ V}$ ), the current values decrease with the increase of ethanol concentration probably due to the increase of ethanol adsorption on the surface [13]. For potentials more

positive than  $0.5 \text{ V}$ , the current values increase with ethanol concentration, even for  $1 \text{ mol l}^{-1}$ . The electrocatalysts performance in ethanol oxidation is strongly dependent of the thermal treatment as shown in Fig. 4. In the region of interest for fuel cell applications ( $0.5$ – $0.7 \text{ V}$ ), the electrocatalysts treated at  $400^\circ\text{C}$  under argon flow has the poor performance and this is probably due to the presence of residual chlorine coming from the decomposition of the PtRu complex under these conditions [9]. It is known that even small residual levels of chlorine in DMFC anode catalysts degrade fuel cell performance [7–9,14,15]. When the electrocatalyst is treated at  $400^\circ\text{C}$  under hydrogen flow, the chlorine is eliminated to the gas phase as hydrogen chloride [9,15] and an

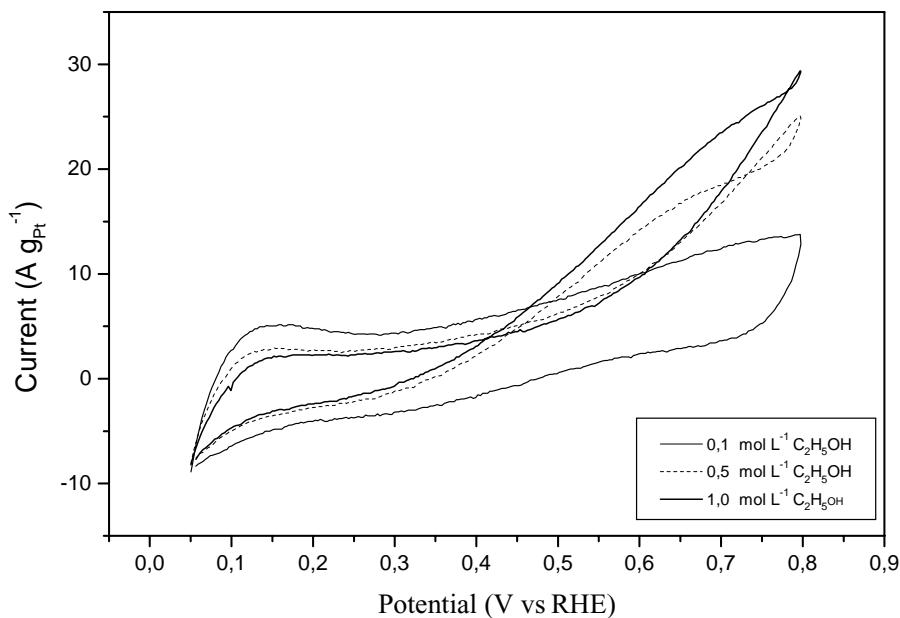


Fig. 3. Cyclic voltammety of the electrocatalyst treated at 400 °C under hydrogen flow and submitted to the oxidative thermal treatment in 0,5 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> with a sweep rate of 10 mV s<sup>-1</sup> with different concentrations of ethanol.

increase in the current values is observed. The electrocatalyst treated at 650 °C under hydrogen flow showed a similar performance to that treated at 400 °C despite the larger particle size. The electrocatalysts treated at 650 °C under argon flow showed a similar performance to the commercial electrocatalyst from E-TEK. The oxidative thermal treatment practically does not modify its performance. Similar results were observed for PtRu/C electrocatalysts activated

at 300 °C in air or nitrogen that showed similar performance for the methanol oxidation [14]. The best performance was obtained using the electrocatalyst treated at 400 °C under hydrogen flow and submitted to the oxidative thermal treatment. The current values were approximately two times greater than the commercial E-TEK electrocatalyst. The treatment under hydrogen flow led to enrichment of platinum on the nanoparticle surface and the major part of the

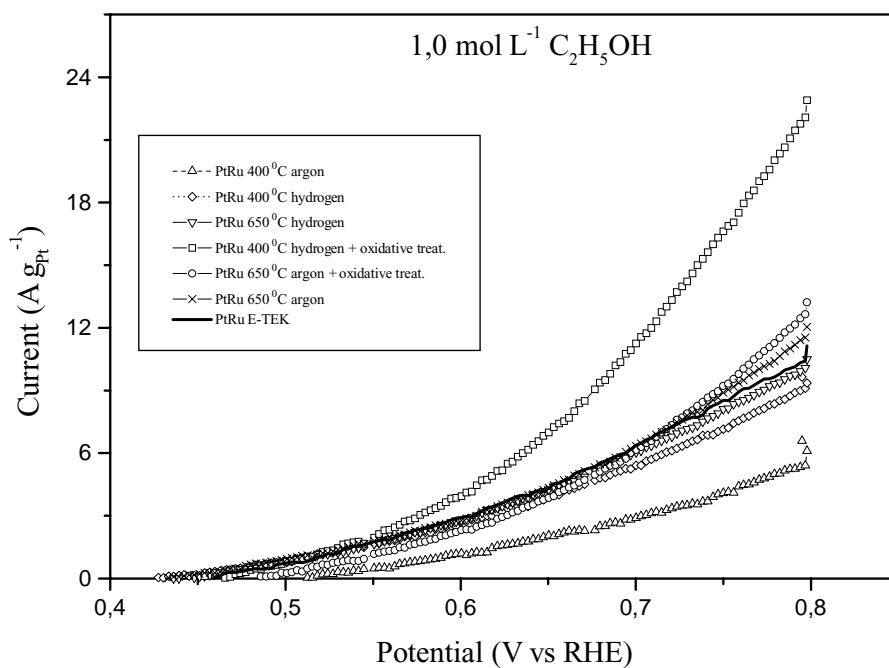


Fig. 4. Cyclic voltammety of the electrocatalysts in 0,5 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 1,0 mol l<sup>-1</sup> of ethanol with a sweep rate of 10 mV s<sup>-1</sup>, considering only the anodic sweep.

ruthenium existed as metallic ruthenium. When submitted to the oxidative thermal treatment, the ruthenium segregated to the surface and oxidized ruthenium species were formed while platinum remained in the metallic form [14,16]. Thus, this electrocatalyst probably had the optimal composition of metallic platinum and oxidized ruthenium species on the PtRu nanoparticle surface, which could be the active species that promotes ethanol oxidation in the bi-functional mechanism proposed for methanol oxidation [11,16–18].

#### 4. Conclusions

The PtRu molecular precursor was suitable for making active PtRu/C electrocatalysts for ethanol electro-oxidation. However, the thermal treatment affected strongly the performance of the catalysts. The electrocatalyst treated under hydrogen flow and submitted to an oxidative thermal treatment had a superior performance. This could be attributed to the better control of the metallic platinum and oxidized ruthenium species present on the PtRu nanoparticle surface developed in this treatment.

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