



Preparation and characterization of Pt–Rare Earth/C electrocatalysts using an alcohol reduction process for methanol electro-oxidation

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ABSTRACT

Pt–Rare Earth/C electrocatalysts (Rare Earth = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho and Er) were prepared by an alcohol reduction process using ethylene glycol as reduction agent and solvent and Vulcan XC72 as support. The electrocatalysts were characterized by energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The electro-oxidation of methanol was studied in acid medium by cyclic voltammetry and chronoamperometry using thin porous coating technique. The XRD patterns indicate that all electrocatalysts present the face-centered cubic (fcc) structure of Pt and the presence of Rare Earth hydroxides. PtEr/C, PtTb/C, PtLa/C, PtDy/C and PtNd/C electrocatalysts prepared by this methodology showed superior performance for methanol electro-oxidation at room temperature compared to Pt/C.

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1. Introduction

Fuel cell 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 hydrogen storage problems, DAFC uses a liquid fuel simplifying the fuel system. Methanol has been considered the most promising fuel, because it is more efficiently oxidized than other alcohols; however, slow anode kinetics are observed [1–4].

In the last years many studies have been made for the development of new Pt electrocatalysts for anodic oxidation of small organic molecules for fuel cell systems, particularly, methanol [5–7]. Tang and Lu [8] prepared PtLnO_x/C catalysts (Ln = Sc, Y, La, Ce, Pr and Nd) by wet precipitation and reduction method. In this methodology, Rare Earth nitrates were dissolved in a mixture of water and ethanol and added to the carbon support, followed by precipitation with sodium carbonate. The obtained materials were calcined at 600 °C to obtain LnO_x/C. Finally, Pt–LnO_x/C catalysts were prepared reducing H₂PtCl₆ with NaBH₄. The electro-oxidation of methanol was studied using cyclic voltammetry and chronoamperometry in acid medium and the results showed that all PtLnO_x/C (except for NdO_x) have better performance than Pt/C.

Díaz et al. [9] prepared different Pt/CeO₂ composite electrodes to study the electrochemical oxidation of methanol and ethanol and concluded that ceria appears to be an effective alternative to ruthenium in direct alcohol fuel cells. The enhancement of alcohol oxidation by CeO₂ was explained by two mechanisms: by inhibiting CO adsorption or by ceria oxygen storage capacity playing a role to ease the oxidation of adsorbed CO. Takahashi et al. [10] synthesized Pt–CeO₂/C using a combined process of precipitation and co-impregnation methods and investigated the activity for methanol oxidation using electrochemical techniques. The current density of the Pt–CeO₂/C anode was much higher than that of Pt–Ru/C alloy at temperatures between 28 and 60 °C and the authors consider this catalyst a promising candidate for direct methanol fuel cells. Wang et al. [11] prepared Pt–CeO₂/CNT by adsorbing Pt nanoparticles on CeO₂-coated carbon nanotubes. Compared to Pt supported on carbon nanotubes, Pt–CeO₂/CNT exhibited higher catalytic activity for methanol oxidation and the corresponding CO stripping potential shifted to a lower value indicating that CeO₂ can make CO electron-oxidation easier.

In this work, Pt–Rare Earth/C electrocatalysts (Rare Earth = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho and Er) were prepared in a single step by an alcohol reduction process [7,12] using ethylene glycol as reduction agent and solvent and Vulcan XC72 as support. The obtained materials were tested for methanol oxidation in acid medium using cyclic voltammetry and chronoamperometry experiments.

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2. Experimental

Pt–Rare Earth/C electrocatalysts (Rare Earth = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho and Er) were prepared (20 wt% and Pt:RE atomic ratio of 60:40) by an alcohol reduction process [7,12] using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich) and Rare Earth(III) chlorides (Aldrich) as metal sources, ethylene glycol as solvent and reducing agent and Vulcan XC72 as support. In a typical procedure, the metal sources were dissolved in ethylene glycol/water (75/25, v/v) and the carbon support was added. After this, a KOH solution 1 mol L^{-1} was added drop a drop under stirring (KOH/Pt + RE molar ratio = 8) and the mixtures were treated in an ultrasound bath for 5 min and submitted to reflux for 3 h under open atmosphere. The mixtures were filtered and the solids washed with water and dried at 70°C for 2 h.

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

XRD analyses were performed using a Rigaku diffractometer model Multiflex with a $\text{Cu K}\alpha$ radiation sources. 2θ angles from 10° to 90° were recorded at a scanning speed of 2° min^{-1} .

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.

Electrochemical studies were carried out using the thin porous coating technique [12–14]. An amount of 20 mg of the electrocatalysts was added to a solution of 50 mL of water containing three drops of a 6% polytetrafluoroethylene (PTFE) suspension. The mixture was treated in an ultrasound bath for 10 min. A quantity of electrocatalysts present in the mixture was transferred to the cavity of the working electrode. The quantity of electrocatalysts in the working electrode was determined with a precision of 0.0001 g. In cyclic voltammetry and chronoamperometry experiments the current values (I) were expressed in amperes and were normalized per gram of platinum (A_{Pt}^{-1}). The quantity of platinum was calculated considering the mass of the electrocatalysts present in the working electrode multiplied by its percentage of platinum. The working electrodes have a geometric area of 0.3 cm^2 with a depth of 0.3 mm. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Cyclic voltammetry and chronoamperometry experiments were performed at 25°C with 1.0 mol L^{-1} of methanol in 0.5 mol L^{-1} H_2SO_4 solutions saturated with N_2 using a Microquimica (model MQPG01, Brazil) potencioestat/galvanostat coupled to a personal computer with Microquimica software.

3. Results and discussion

Pt–Rare Earth/C where prepared in a single step by an alcohol reduction process taking in account the following facts: as the reduction potential of Ln elements is about 3.5 V negative of that for Pt [6] and ethylene glycol is a mild reducing agent, it was not possible to reduce Rare Earth(III) ions in the conditions used in the chosen methodology. On the other hand, if the electrocatalysts were prepared in alkaline medium (KOH/Pt–Rare Earth molar ratio of 8), Rare Earth(III) ions could be deposited on the carbon support as Rare Earth oxide–hydroxide and Pt(IV) ions, which were reduced by ethylene glycol also in basic conditions, as metallic Pt. In a previous work [7] we have prepared PtLa/C electrocatalysts with different Pt:La atomic ratios (60:40, 70:30 and 90:10) and found that the electrocatalyst prepared with Pt:La atomic ratio of 60:40 showed the better performance for methanol oxidation than others. In this work, different Pt–Rare Earth/C electrocatalysts were prepared with Pt:RE atomic ratio of 60:40 (Table 1). The EDX analysis showed that the Pt:RE atomic ratios obtained for all electrocatalysts were similar to the ones used in the preparations.

The X-ray diffractograms of Pt/C and Pt–Rare Earth/C electrocatalysts are shown in Fig. 1. In all diffractograms it was observed a broad peak at about 25° associated with the Vulcan XC72 support material and five peaks at approximately $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$ and 87° , which are associated with the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes, respectively, of the face-centered cubic (fcc) structure characteristic of platinum and platinum alloys [13,14]. As described before, it was not possible to reduce the Rare Earth ions in the used conditions. Thus, it seems improbable the formation of Pt–Rare Earth alloys. For PtLa/C, PtPr/C, PtNd/C and PtCe/C it was also observed one peak at approximately 28° that could be

Table 1

Pt:RE atomic ratios obtained by EDX and average particle size of the Pt–Rare Earth/C electrocatalysts (metal loading 20 wt%, Pt:RE atomic ratio of 60:40)

Electrocatalysts	Atomic ratio—EDX, Pt:RE	Particle size (nm)
PtLa/C	60:40	6
PtCe/C	59:41	10
PtPr/C	70:30	10
PtNd/C	62:38	7
PtSm/C	55:45	10
PtTb/C	67:33	10
PtDy/C	60:40	10
PtHo/C	64:36	10
PtEr/C	65:35	10
Pt/C	–	3

attributed to Rare Earth(III) hydroxides (plane 1 1 0 and relative intensity of 100%) [15,16]. In a previous work [7] we have already prepared La/C catalyst by the methodology used in this work and observed in the X-ray diffractogram the formation of $\text{La}(\text{OH})_3$ as product. The presence of Rare Earth hydroxides was not clear in the other diffractograms, which indicated that they could have an amorphous structure. Similar results were also observed by Tang and Lu for PtLnO_x/C catalysts [7]. The average particle size was calculated using the Scherrer equation using the reflections of Pt(2 2 0) peak [17] and the values for Pt–Rare Earth electrocatalysts were in the range of 6–10 nm. However, the average particle size of the Pt/C electrocatalyst was found to be 3.0 nm and it was smaller than that of the Pt–Rare Earth/C electrocatalysts, consequently for syntheses of Pt–Rare Earth/C electrocatalysts is necessary to modify our electrocatalysts preparation methodology to decrease the Pt particle size. TEM micrograph of PtLa/C electrocatalyst (Fig. 2) showed the Pt particles with sizes of $6.5 \text{ nm} \pm 2.5 \text{ nm}$ and a good distribution on the carbon support.

The cyclic voltammogram curves of Pt/C E-TEK, PtLa/C, PtEr/C, PtTb/C and PtRu/C electrocatalysts in 0.5 mol L^{-1} H_2SO_4 and 1.0 mol L^{-1} of methanol are shown in Fig. 3.

For Pt–Rare Earth/C electrocatalysts the oxidation of methanol started at approximately 0.5 V, which is similar to the values observed by Tang and Lu [8], and the current values were greater than Pt/C electrocatalyst. PtTb/C showed better performance than PtEr/C and PtLa/C electrocatalysts. For PtRu/C electrocatalysts prepared by the same methodology, the electro-oxidation of methanol started at approximately 0.3 V and the current values in the potential range of 0.3–0.5 V were higher than the Pt–Rare Earth/C catalysts. On the other hand, above 0.5 V, PtTb/C and PtEr/C

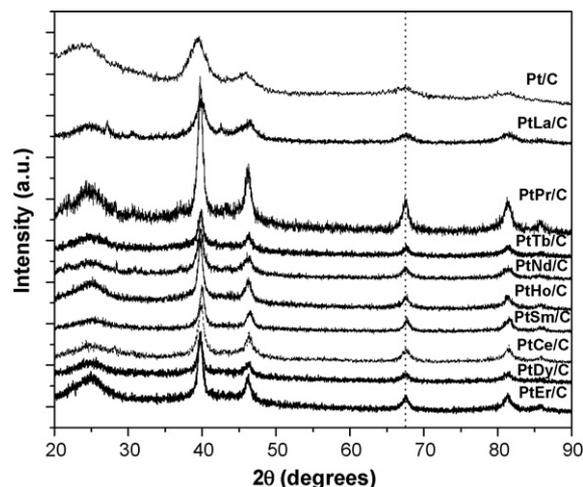


Fig. 1. X-ray diffractograms of Pt/C and Pt–Rare Earth/C electrocatalysts.

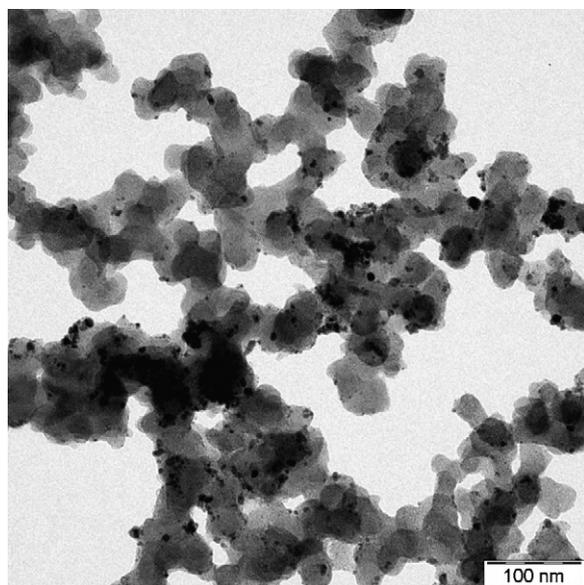


Fig. 2. Transmission electron micrograph of PtLa/C electrocatalyst.

electrocatalysts showed higher current values than PtRu/C electrocatalyst.

The chronoamperometry experiments were carried out to examine the electrochemical stability of the electrocatalysts (Fig. 4).

The results were obtained in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and $1.0 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ at an anodic potential of 0.5 V versus RHE. This potential is chosen because it is a potential of interest to be applied in direct methanol fuel cell. In all chronoamperometric curves there is a sharp initial current drop in the first 2 min and then the current values practically remain constant until 30 min. The current values obtained for PtEr/C, PtTb/C and PtLa/C electrocatalysts were always higher than those obtained for Pt/C in agreement with cyclic voltammetry experiments; on the other hand, the performance of PtRu/C electrocatalyst was superior to the others.

The final current values at 30 min during chronoamperometry studies are shown in Fig. 5 for Pt/C and Pt–Rare Earth/C electrocatalysts.

The final current values after holding the cell potential at 0.5 V versus RHE for 30 min are following: PtEr/C > PtTb/C > PtLa/C > PtNd/C > PtDy/C > Pt/C > PtPr/C > PtHo/C > PtSm/C > PtCe/C. As already observed by Tang and Lu [8] the addition of Rare Earth elements to

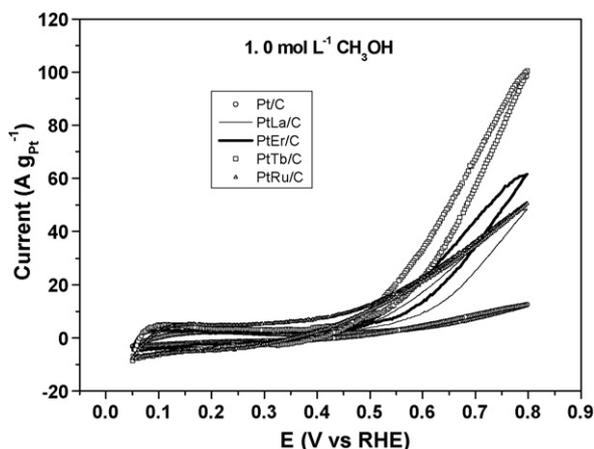


Fig. 3. Cyclic voltammetry of Pt/C, PtRu/C, PtLa/C, PtTb/C and PtEr/C electrocatalysts in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and 1.0 mol L^{-1} of methanol with sweep rate of 10 mV s^{-1} .

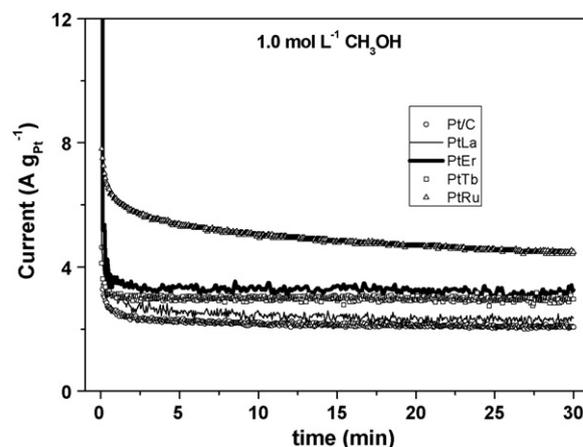


Fig. 4. Current–time curves at 0.5 V in $1.0 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ solution in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ for Pt/C, PtRu/C, PtLa/C, PtEr/C and PtTb/C electrocatalysts.

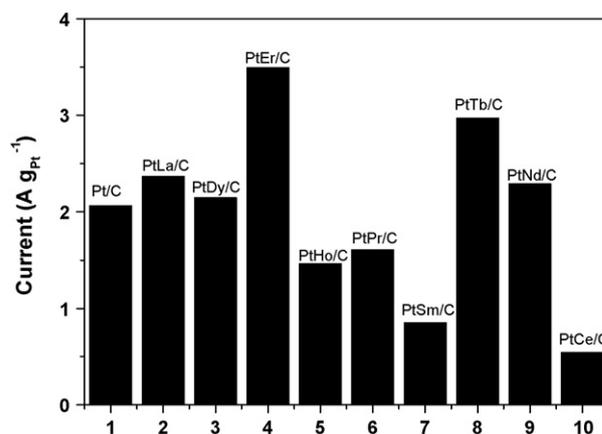


Fig. 5. Current density values at 1800 s during chronoamperometry experiments for Pt/C and Pt–Rare Earth/C electrocatalysts.

Pt/C could increase the catalytic activity for methanol oxidation. On the other hand, they found that PtPrO_x/C was the best electrocatalyst for methanol oxidation, which is in contrast with our results. Probably, these differences could be explained by different methods of catalyst preparation and different Pt:Rare Earth (3:1) atomic ratios used.

As reported by other authors [8–11] the superior activity for methanol oxidation of Pt–Rare Earth/C compared to Pt/C electrocatalyst probably could be attributed to the bi-functional mechanism where Pt acts on methanol adsorption and dissociation and the Rare Earths provide oxygenated species at lower potentials for oxidative removal of adsorbed CO.

4. Conclusions

Active Pt–Rare Earth/C electrocatalysts for methanol oxidation could be prepared by alcohol-reduction process in alkaline medium. The X-ray diffractogram of Pt–Rare Earth/C electrocatalysts showed the typical fcc structure of platinum and the presence of Rare Earth(III) hydroxides. In the studied conditions PtEr/C, PtTb/C, PtLa/C, PtNd/C and PtDy/C electrocatalysts showed higher current values than Pt/C in the potential range of interest for direct methanol fuel cell ($0.2\text{--}0.6 \text{ V}$). Further work is necessary to modify our electrocatalysts preparation methodology to decrease the Pt particle size and to improve the catalysts activity as well, to prepare carbon-supported PtRu in the presence of Rare Earths that

seems very promising for methanol oxidation [18,19]. Experiments are under way.

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