Ionics (2008) 14:577–581
DOI 10.1007/s11581-008-0212-5

SHORT COMMUNICATION

Electrooxidation of ethanol using Pt rare earth–C electrocatalysts prepared by an alcohol reduction process

Almir Oliveira Neto · André Y. Watanabe · Rita M. de S. Rodrigues · Marcelo Linardi · Christina A. L. G. O. Forbicini · Estevam V. Spinacé

Received: 21 November 2007 / Accepted: 8 February 2008 / Published online: 5 March 2008

Abstract Pt rare earth–C electrocatalysts (rare earth = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho, Er, Tm, and Lu) were prepared by an alcohol reduction process using ethylene glycol as reduction agent and solvent and Vulcan XC 72 as support. The electrocatalysts were characterized by energy-dispersive X-ray analysis, X-ray diffraction (XRD), and cyclic voltammetry. The electrooxidation of ethanol 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 structure of Pt and the presence of rare earth hydroxides. All electrocatalysts prepared by this methodology showed superior performance for ethanol electrooxidation at room temperature compared to Pt–C.

Keywords Pt rare earth–C · Alcohol reduction process · Ethanol oxidation · Fuel cell

Introduction

Fuel cell employing alcohols directly as combustible (direct alcohol fuel cell) are attractive as power sources for mobile, stationary, and portable applications. Methanol has been considered the most promising fuel because it is more efficiently oxidized than others alcohols; however, slow anode kinetics is observed and it is considered as a toxic product. Ethanol offers an attractive alternative in relation to methanol as a fuel in low-temperature fuel cells because it can be produced in large quantities from agricultural products and it is the major renewable biofuel from the fermentation of biomass. However, its complete oxidation to CO_2 is more difficult than that of methanol due to the difficulty in C–C bond breaking and to the formation of CO intermediates that poison the platinum anode catalysts. In this context, more active electrocatalysts are essential to enhance the ethanol electrooxidation [1–4].

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 ethanol fuel cell. Platinum itself is known to be rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption of ethanol. Efforts to mitigate the poisoning of Pt have been concentrated on the addition of cocatalysts to platinum. In recent years, it is found that certain metal oxides, such as RuO_2, SnO_2, and CeO_2, can enhance the catalytic activity for ethanol and methanol electrooxidation through synergetic interaction with Pt [5, 6].

Rare earth (RE) oxides exhibit a number of characteristics that make them interesting for catalytic studies. Recently, Tang and Lu [7] 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 H_2PtCl_6 with $NaBH_4$. The electrooxidation 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.

A. O. Neto (✉) · A. Y. Watanabe · R. M. d. S. Rodrigues · M. Linardi · C. A. L. G. O. Forbicini · E. V. Spinacé (✉)
Instituto de Pesquisas Energéticas e Nucleares, IPEN—CNEN/SP,
Av. Prof. Lineu Prestes, 2242—Cidade Universitária,
CEP 05508-000 São Paulo, São Paulo, Brazil
e-mail: aolivei@ipen.br
e-mail: espinace@ipen.br

In this work, Pt rare earth–C electrocatalysts (rare earth = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho Er, Tm, and Lu) prepared in a single step by an alcohol reduction process were tested for ethanol electrooxidation in acid medium using cyclic voltammetry and chronoamperometry.

Experimental

Pt rare earth–C electrocatalysts (rare earth = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho, Er, Tm, and Lu) were prepared (20 wt.% and Pt-to-RE atomic ratio of 50:50) by an alcohol reduction process [8] using $H_2PtCl_6.6H_2O$ (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 $(KOH/Pt + RE = 8)$ 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 energy-dispersive X-ray (EDAX) analysis using a scanning electron microscope Philips XL30 with a 20-keV electron beam and provided with EDAX DX-4 microanalyzer.

X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Multiflex with CuKα radiation sources. The 2 angles from 10° to 90° were recorded at a scanning speed of 2 min^{-1}.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [9]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing three drops of a 6% polytetrafluoroethylene suspension. The resulting mixture was treated in an ultrasound bath, filtered, and transferred to the cavity (0.15 mm deep and 0.36-cm^2 area).

Table 1 Pt-to-RE atomic ratios obtained by EDAX and mean particle size of the Pt rare earth–C electrocatalysts (metal loading 20 wt.%, Pt-to-RE atomic ratio of 50:50)

Eletrocatalysts	Atomic ratio–EDAX Pt to 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
PtTm–C	73:27	15
PtLu–C	53:47	10
Pt–C E-TEK	–	3

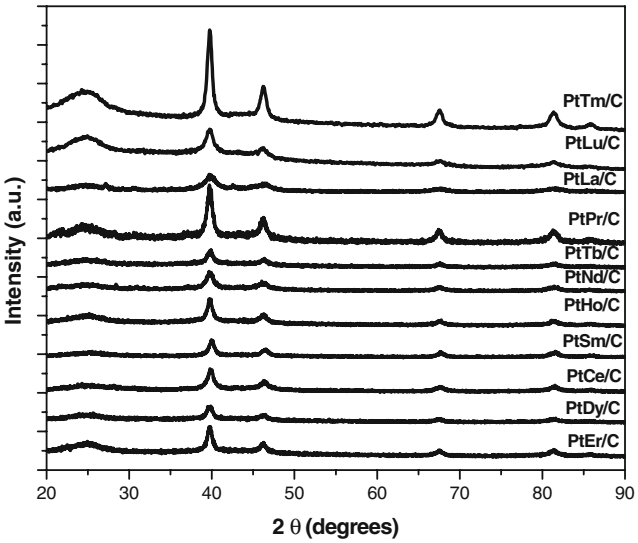

Fig. 1 X-ray diffractograms of Pt rare earth–C electrocatalysts

In cyclic voltammetry and chronoamperometry experiments, the currents values (I) were expressed in amperes and were normalized (Ag_{Pt}^{-1}) per gram of platinum [10, 11]. The quantity of platinum was calculated considering the mass of the electrocatalyst present in the working electrode multiplied by its percentage of platinum. The reference electrode was a reversible hydrogen electrode (RHE) and the counter electrode was a platinized Pt plate. Electrochemical measurements were made using a Microquimica (model MQPG01, Brazil) potentiostat–galvanostat coupled to a personal computer with Microquimica software. Cyclic voltammetry and chronoamperometry were used to evaluate the ethanol oxidation and the experiments were performed at room temperature in a 1.0 mol L^{-1} of ethanol in 0.5-mol L^{-1} H_2SO_4 solutions saturated with N_2.

Results and discussion

Pt rare earth–C electrocatalysts were prepared in a single step by an alcohol reduction process taking in account the following facts: as the reduction potential of Lanthanides 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 using ethylene glycol. On the other hand, if Pt rare earth–C 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 [8], we have prepared PtLa–C electrocatalysts with different Pt-to-La

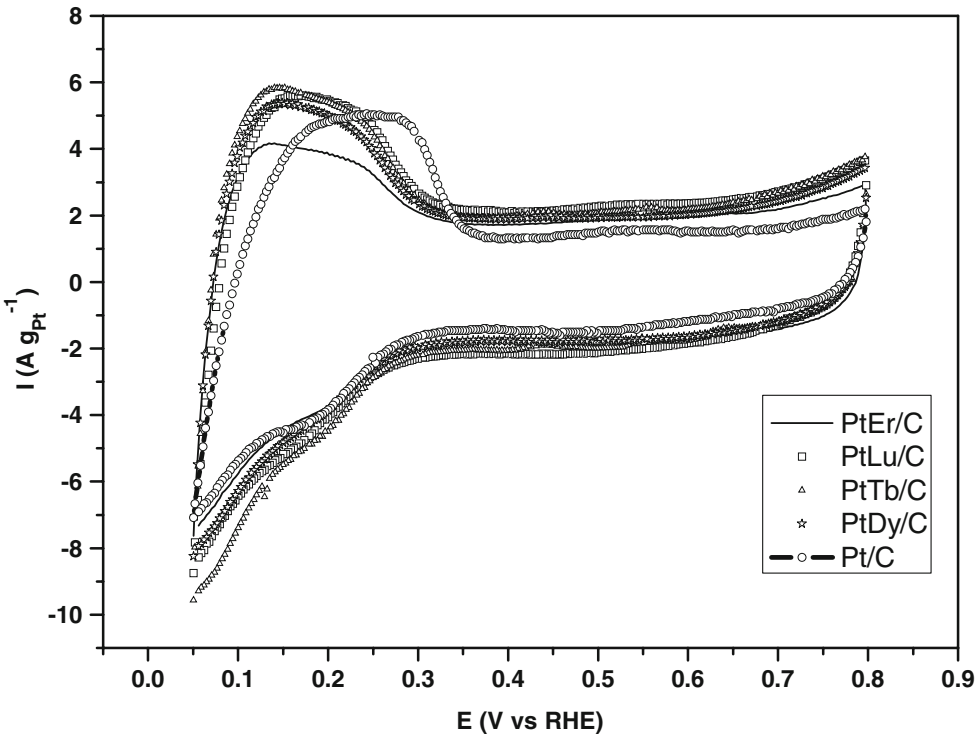

Fig. 2 Cyclic voltammetry of Pt rare earth–C electrocatalysts in 0.5 mol L^{-1} H_2SO_4 with a sweep rate of 10 mV s^{-1}

atomic ratios (50:50, 70:30, and 90:10) and found that the electrocatalyst prepared with Pt-to-La atomic ratio of 50:50 showed the better performance for methanol oxidation than others. In this work, different Pt rare earth–C electrocatalysts were prepared with Pt-to-RE atomic ratio of 50:50 (Table 1). The EDAX analysis showed that the Pt-to-RE atomic ratios obtained for all electrocatalysts were approximately 60:40 and were similar to the ones used in the preparations.

The X-ray diffractograms of Pt rare earth–C electrocatalysts are shown in Fig. 1. In all diffractograms, it was observed that a broad peak at about 25° was associated with

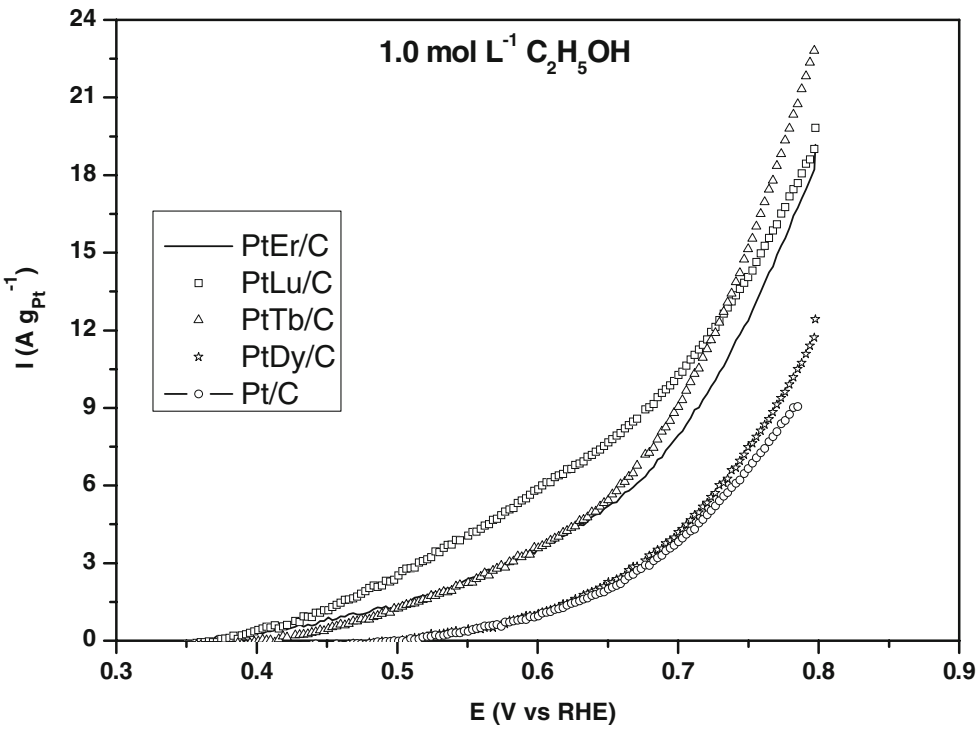

Fig. 3 Cyclic voltammetry of Pt rare earth–C electrocatalysts in 0.5 mol L^{-1} H_2SO_4, containing 1.0 mol $L^{-1}$of ethanol with a sweep rate of 10 mV s^{-1}, considering only the anodic sweep

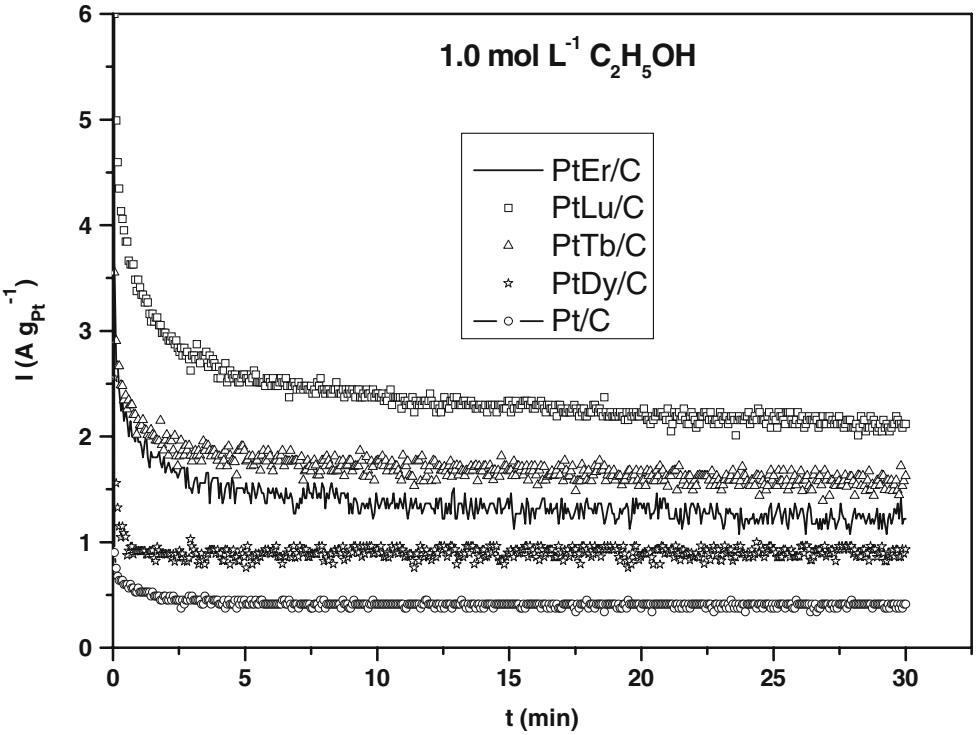

Fig. 4 Current–time curves at 0.5 V in 1-mol L^{-1} ethanol solution in 0.5 mol L^{-1} H_2SO_4 for Pt–C, PtEr–C PtTb–C, PtLu–C, and PtDy–C eletrocatalysts

the Vulcan XC72 support material and five peaks at approximately 2θ=40°, 47°, 67°, 82°, and 87°, which are associated with the (111), (200), (220), (311), and (222) planes, respectively, of the face-centered cubic (fcc) structure characteristic of platinum and platinum alloys [10, 11]. For PtLa–C, PtPr–C, PtNd–C, and PtCe–C, one peak was also observed at approximately 28° that could be attributed to rare earth(III) hydroxides (plane 110 and relative intensity of 100%) [12, 13]. In a previous work [8], we have already prepared La–C catalyst by the methodology used in this work and the formation of La $(OH)_3$ as product was observed in the X-ray diffractogram. In the other diffractograms, the presence of rare earth hydroxides was not clear, 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

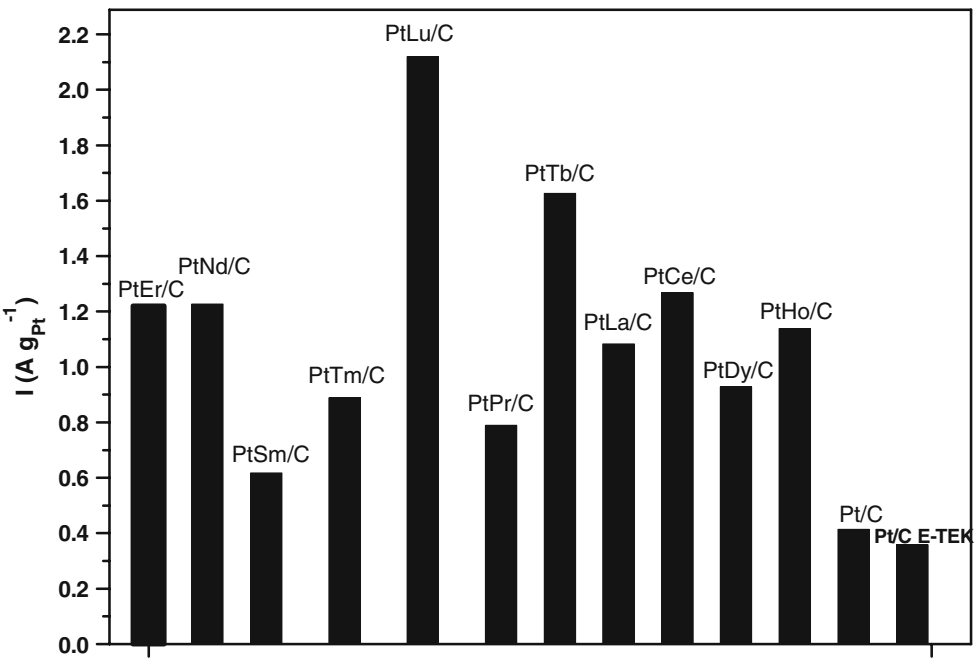

Fig. 5 Current density values at 1,800 s during chronoamperometry experiments for Pt–C and Pt rare earth–C eletrocatalysts

average crystallite sizes were calculated from the XRD peak broadening of Pt(220) peak using Scherrer equation [14] and the values are in the range of 6–15 nm.

The cyclic voltammogram (CV) curves of Pt–C, PtEr–C, PtDy–C, PtLu–C, and PtTb–C eletrocatalysts in the absence of ethanol are shown in Fig. 2. All CV do not have a well-defined hydrogen adsorption–desorption region (0–0.4 V). The CV of Pt rare earth–C electrocatalysts showed an increase in the currents in the double layer (0.4–0.8 V) in relation to the Pt–C, which may be attributed the formation of rare earth oxide species. Analysis of the cathodic scan also showed an increase in the currents in the double layer that could be associated with the reduction of rare earth oxide species in the catalyst.

The Pt rare earth–C electrocatalysts performances in 1.0 mol L^{-1} of ethanol are shown in Fig. 3. The anodic cyclic voltammetry responses were plotted after subtracting the background currents and the current values were normalized per gram of platinum, considering that ethanol adsorption and dehydrogenation occur only on platinum sites at ambient temperature [10, 11]. For Pt–C electrocatalyst, ethanol electrooxidation started at approximately 0.5 V while for PtLu–C, PtTb–C, and PtEr–C electrocatalysts the onset potential was shifted negatively by about 100 mV and the current values were higher than that of Pt–C catalyst in all range of potential. The Pt rare earth–C eletrocatalysts performances for ethanol oxidation were also studied by chronoamperometry (Fig. 4). The chronoamperometry experiments were carried out to examine the electrochemical stability of eletrocatalysts. The results were obtained in 0.5 mol L^{-1} H_2SO_4 and 1.0 mol L^{-1} C_2H_5OH at an anodic potential of 0.5 V versus RHE. In all chronoamperometric curves, there is a sharp initial current drop in the first 3 min and then the current values practically remain constant until 30 min. The current values obtained for Pt rare earth–C electrocatalysts were always higher than those obtained for Pt–C in agreement with cyclic voltammetry experiments. The final current values (Fig. 5) after holding the cell potential at 0.5V versus RHE for 30 min are the following: PtLu–C> PtTb–C > PtEr–C ≈ PtNd–C ≈ PtCe–C > PtHo–C > PtLa–C >PtDy–C > PtTm–C > PtPr–C > PtSm–C > Pt–C. Similar results were obtained by Tang and Lu [7], who found that the addition of rare earth elements to Pt–C could increase the catalytic activity of methanol oxidation.

The superior activity of Pt rare earth–C electrocatalysts compared to Pt–C electrocatalyst probably could be attributed to the bifunctional mechanism were Pt acts on ethanol adsorption and dissociation and rare earth provides oxygenated species at lower potentials for oxidative removal of adsorbed CO.

Conclusions

Active Pt rare earth–C electrocatalysts for ethanol oxidation could be prepared by alcohol reduction process in alkaline medium. The X-ray diffractograms of Pt rare earth–C electrocatalysts showed the typical fcc structure of platinum and the presence of rare earth (III) hydroxides. All Pt rare earth–C electrocatalysts showed higher current values than Pt–C in the potential range of interest for direct ethanol fuel cell (0.2–0.6 V). Further work is necessary to modify the electrocatalyst preparation methodology in order to decrease the Pt particle size and investigate these electrocatalysts in gas diffusion electrodes for tests in single direct ethanol fuel cell.

Acknowledgement The authors thank the Fundo Setorial de Energia 504795/2004-0, the Foundation for Research Support of the State of São Paulo, and the National Council for Scientific and Technological Development for financial support.

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