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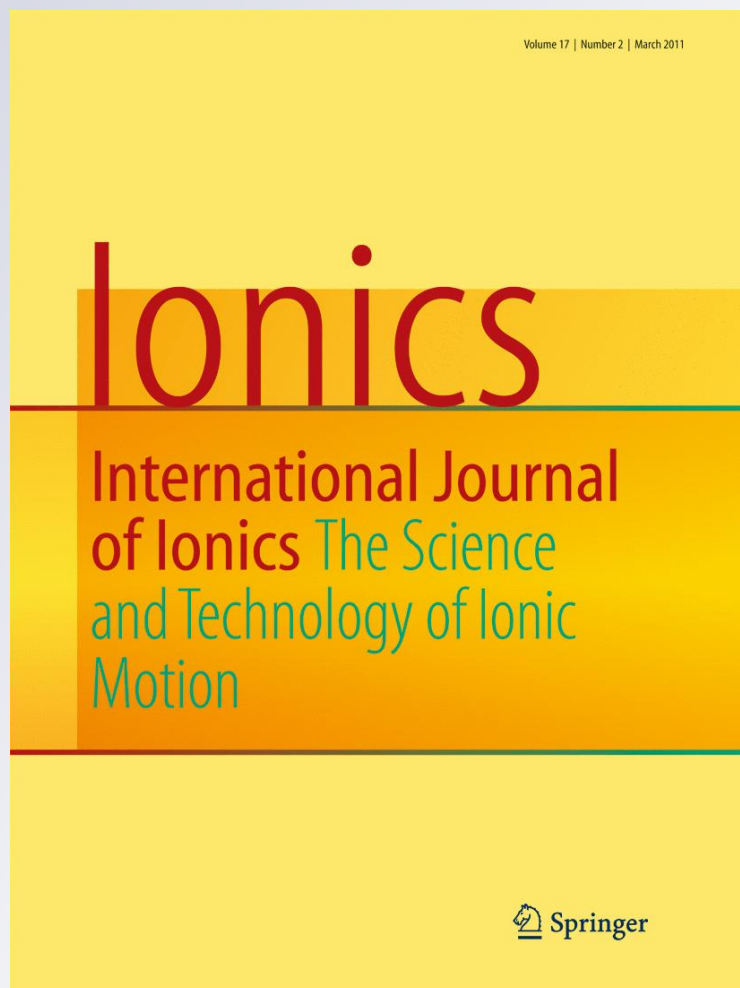
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Preparation and characterization of PtRu/C-rare earth using an alcohol-reduction process for ethanol electro-oxidation

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Abstract PtRu/C (100% C) and PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃, and PtRu/C-Er₂O₃ (85% C and 15% rare earth) electrocatalysts were prepared in a single step by an alcohol-reduction process using H₂PtCl₆ · 6H₂O and RuCl₃ · xH₂O as metal sources, ethylene glycol as solvent and reducing agent, Vulcan XC72 and rare earth (RE) as support. The electrocatalysts were characterized by energy dispersive X-ray, X-ray diffraction, and transmission electron microscopy. The performance for ethanol oxidation was investigated by cyclic voltammetry and chronoamperometry at room temperature, and studies on the direct ethanol fuel cell were carried at 100 °C. The Pt:Ru atomic ratios were similar to the nominal used in preparation, and the average particle sizes were in the range of 2.0–3.0 nm. All PtRu/C-RE electrocatalysts showed an increase of performance for ethanol oxidation at room temperature and also on a single direct ethanol fuel cell tests in relation to PtRu/C electrocatalyst at 100 °C.

Keywords PtRu/C-rare earth electrocatalyst · Alcohol-reduction process · Ethanol oxidation · Direct ethanol fuel cell

Introduction

Recently, there has been an increasing interest in the development of direct alcohol fuel cells (DAFCs), because

the storage of the liquid fuel is much easier than gas fuel [1, 2]. The ethanol have all been considered as the most promising fuel in a DAFCs, because it is produced in large quantities from biomass and is much less toxic than methanol [3, 4]. However, its complete oxidation to CO₂ is more difficult than that of methanol due to the difficulties in C–C bond breaking and the formation of intermediates that poison the platinum anode catalysts [5, 6]. The Pt/C electrocatalysts is commonly used as anode in low-temperature fuel cells; however, platinum alone is not a good catalyst for the ethanol oxidation reaction; hence, the addition of co-catalysts to platinum is necessary [7–11]. In recent years, it is found that certain metal oxides, such as CeO₂, RuO₂, or SnO₂, can enhance the catalytic activity for ethanol electro-oxidation through synergetic interaction with Pt [12–17]. In order to enhance the efficiency and reduce the catalyst price, Pt-based bimetallic or multimetallic catalysts have been widely studied, and PtRu or PtSn are the most active catalysts for methanol or ethanol oxidation. The Pt sites act as adsorption and dehydrogenation centers for ethanol, while ruthenium or tin sites provide oxygen-containing species at lower potentials than those on a pure Pt surface.

However, some studies comparing the electrocatalytic activity of PtRu and PtSn catalysts for ethanol electro-oxidation have shown contradictory results [7, 16]. Colmati et al. [7] showed that the activity for ethanol oxidation was higher on PtRu than on Pt₃Sn at room temperature, while Neto et al. [16] showed that PtSn/C was more active than PtRu/C.

The PtRu/C electrocatalysts have some attractive properties, but they still exhibit significant over potentials for the oxidation of small organic molecules; consequently, it is necessary to develop new and more efficient PtRu/C electrocatalysts [6]. It has been described that the addition of a third element to PtRu/C electrocatalyst could increase its activity

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for ethanol oxidation [6]. The addition of rare earth (RE) oxides to PtRu/C could be an alternative interesting for ethanol oxidation, because REs exhibit a number of characteristics that make them interesting for catalytic studies [18, 19].

The aim of this work was to prepare PtRu/C, PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃ and PtRu/C-Er₂O₃ electrocatalysts by alcohol-reduction process substituting part of the carbon support by RE. The obtained materials were tested for ethanol oxidation using electrochemical techniques, and the catalysts also were tested in direct ethanol fuel cell.

Experimental

The atomic composition of the electrocatalysts was chosen to be close to PtRu/C (50:50), the most active composition for the ethanol electro-oxidation reaction [16]. Then PtRu/C (50:50 catalyst metal; 100% C as support) and PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃, and PtRu/C-Er₂O₃ (50:50 catalyst metal; 85% C and 15% RE as support) electrocatalysts were prepared with metal loading of 20 wt. % in a single step by an alcohol-reduction process using H₂PtCl₆·6H₂O (Aldrich) and RuCl₃·xH₂O (Aldrich) as metal sources, ethylene glycol as solvent and reducing agent, Vulcan XC72 and RE (Aldrich) as support. In a typical procedure, the metal sources were dissolved in ethylene glycol/water (75/25, v/v), and the supports were added. The resulting mixtures were treated in an ultrasound bath and were refluxed 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 Pt:Ru atomic ratios were obtained by energy-dispersive X-ray (EDX) analysis using a scanning electron microscope Philips XL30 working a 20 kV and equipped with EDAX DX-4 microanalyser XL30. The X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using Cu K α radiation source ($\lambda=0.15406$ nm). The diffractograms were recorded from $2\theta=20^\circ$ to 90° with a step size of 0.05° and a scan time of 2 s/step. Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100 electron microscope operated at 200 kV. The particle size distributions were determined by measuring the nanoparticles from micrographs using Image Tool Software.

Cyclic voltammetry (CV) and chronoamperometry experiments were performed at 25 °C with 1.0 mol L⁻¹ of ethanol in 0.5 mol L⁻¹ H₂SO₄ solutions saturated with N₂ using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat and the thin porous coating technique [19]. The reference electrode was a RHE and the counter electrode was a platinumized Pt plate.

Table 1 Nominal atomic ratio, atomic ratio obtained by EDX, and crystallite size of the PtRu/C (50:50 catalyst metal; 100% C as support) and PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃, and PtRu/C-Er₂O₃ (50:50 catalyst metal; 85% C and 15% RE as support)

Electrocatalysts	Nominal atomic ratio	EDX atomic ratio	Crystallite size (nm)
PtRu/C	50:50	50:50	2.6
PtRu/C-Er ₂ O ₃	50:50	49:51	<2.0
PtRu/C-Nd ₂ O ₃	50:50	49:51	<2.0
PtRu/C-CeO ₂	50:50	52:48	2.1
PtRu/C-La ₂ O ₃	50:50	49:51	3.0

The direct ethanol fuel cell performances were determined in a single cell with an area of 5 cm². The temperature was set to 100 °C for the fuel cell and 80 °C for the oxygen humidifier. The fuel was 2 mol L⁻¹ 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. The membrane electrode assemblies was prepared by hot pressing a pretreated Nafion®117 membrane, placed between either a PtRu/C, PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃, and PtRu/C-Er₂O₃ electrocatalysts prepared in this work as anode (1 mg Pt cm⁻² catalyst loading) and a 20 wt.% Pt/C E-TEK as cathode (1 mg Pt cm⁻² catalyst loading) at 125 °C for 2 min under a pressure of 225 Kgf cm⁻².

Results and discussion

The Pt:Ru nominal atomic ratios, atomic ratios obtained by EDX, and mean particle size of the prepared electro-

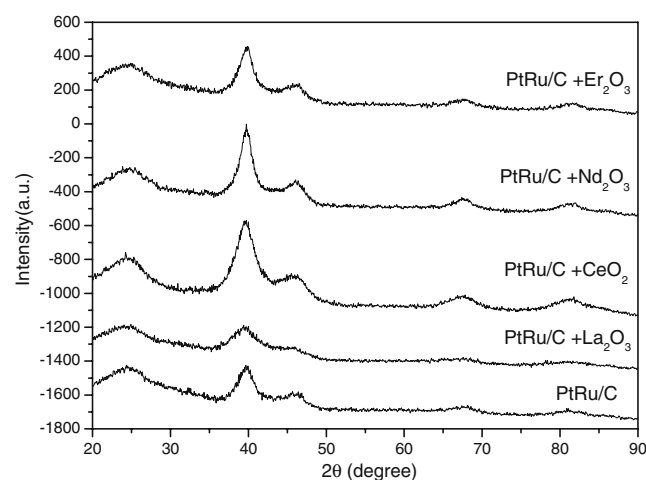
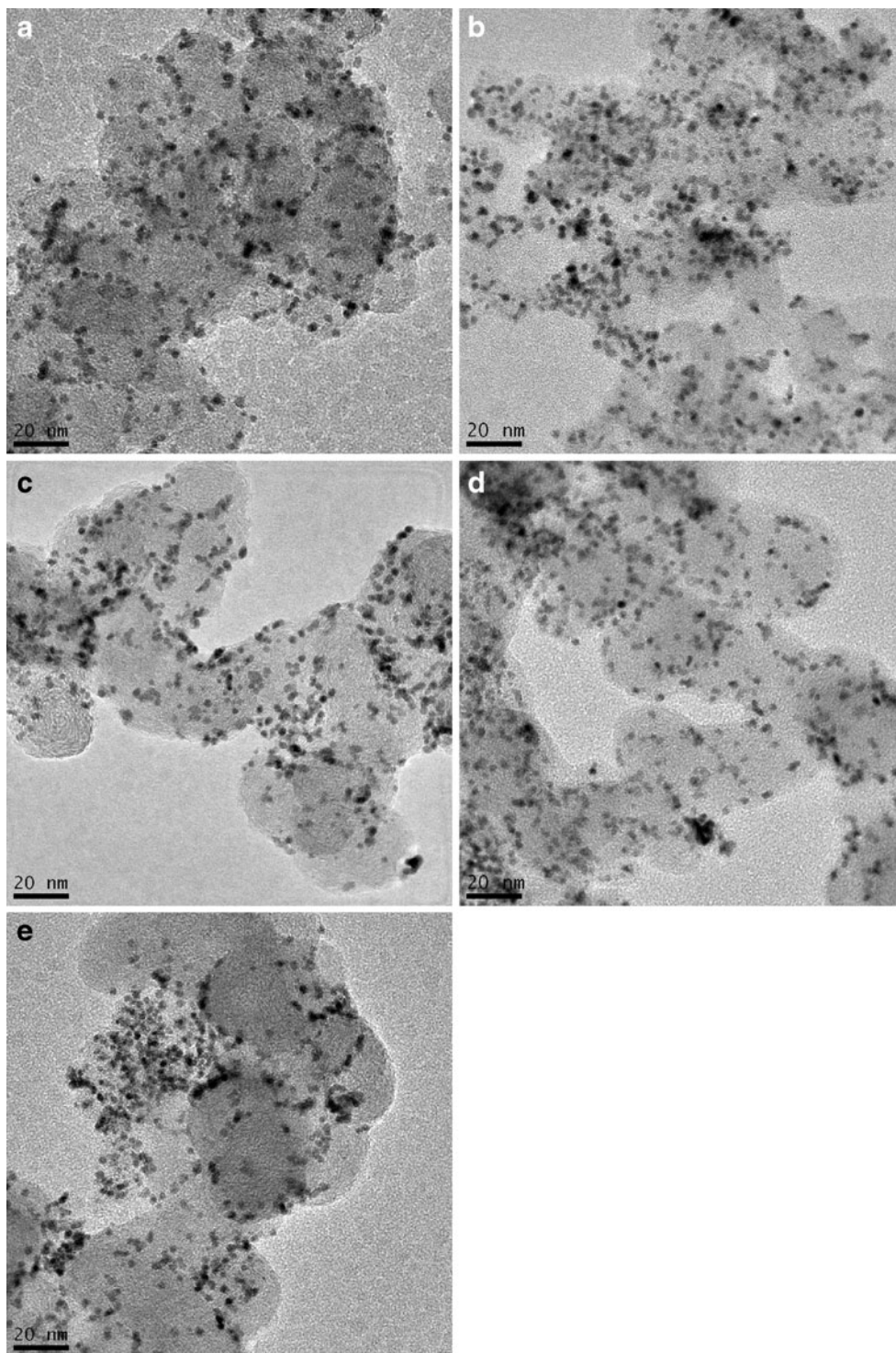


Fig. 1 X-ray diffractograms of PtRu/C (50:50 catalyst metal; 100% C as support) and PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃, and PtRu/C-Er₂O₃ (50:50 catalyst metal; 85% C and 15% RE as support)

catalysts are present in Table 1. The (220) reflections of Pt (fcc) crystalline structure (Fig. 1) were used to calculate the average crystallite sizes using the Scherrer equation [16]. The calculated values using the Scherrer equation were in the range of 2.0–3.0 nm, and all Pt:Ru atomic ratios of the obtained electrocatalysts were similar to the nominal atomic ratios used in the preparation. The X-ray diffractograms of the

PtRu/C (50:50 catalyst metal; 100% C as support) and PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃, and PtRu/C-Er₂O₃ (50:50 catalyst metal; 85% C and 15% RE as support) electrocatalysts are shown in Fig. 1. In all diffractograms, a broad peak at about 25° was associated with the Vulcan XC72 support material. The diffractogram of all electrocatalysts showed peaks at approximately $2\theta=40^\circ$, 47° , 67° , and 82° ,

Fig. 2 Transmission electron micrographs of: PtRu/C (a), PtRu/C-CeO₂ (b), PtRu/C-La₂O₃ (c), PtRu/C-Nd₂O₃ (d), and PtRu/C-Er₂O₃ (e)



which are associated with the (111), (200), (220), and (311) planes, respectively of the face-centered cubic (fcc) structure characteristic of platinum and platinum alloys. No peaks corresponding to a metallic ruthenium, ruthenium oxide phase, CeO_2 , Er_2O_3 , La_2O_3 or Nd_2O_3 , were observed. Figure 2 shows TEM micrographs of PtRu/C (Fig. 2a), PtRu/C- CeO_2 (Fig. 2b), PtRu/C- La_2O_3 (Fig. 2c), PtRu/C- Nd_2O_3 (Fig. 2d), and PtRu/C- Er_2O_3 (Fig. 2e). PtRu/C-RE electrocatalysts (Fig. 2) showed the particles with sizes of 2.0 ± 1.0 nm and a good distribution on the carbon support, which is in agreement with XRD results. Similar results were observed by Huanqiao et al. [1] in the preparation of PtRu/C electrocatalysts using ethylene glycol as reducing agent. The small particle sizes of the nanoparticles were attributed to the stabilizing effect of the ethylene glycol that prevents their agglomerations [1].

Figure 3 shows the CV of PtRu/C (50:50 catalyst metal; 100% C as support) and PtRu/C- CeO_2 , PtRu/C- La_2O_3 , PtRu/C- Nd_2O_3 , and PtRu/C- Er_2O_3 (50:50 catalyst metal; 85% C and 15% RE as support) obtained in a half cell at a scan rate of 10 mV s^{-1} between 0.05 and 0.8 V in 1.0 mol L^{-1} of ethanol and $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. The electro-oxidation of ethanol started at approximately 0.35 V for PtRu/C- CeO_2 , PtRu/C- Nd_2O_3 , and PtRu/C- La_2O_3 , while for PtRu/C- Er_2O_3 and PtRu/C electrocatalysts, the electro-oxidation of ethanol started at approximately 0.45 V. PtRu/C- CeO_2 and PtRu/C- La_2O_3 (50:50) showed the best activity in comparison to the other electrocatalysts. These results confirm the beneficial effect of adding RE systems in the synthesis of PtRu. Neto et al. [20] and Zhou et al. [10] also showed the enhancement of activity for ethanol electro-oxidation resulting from the addition of CeO_2 to platinum–tin catalysts or CeO_2 to platinum. These

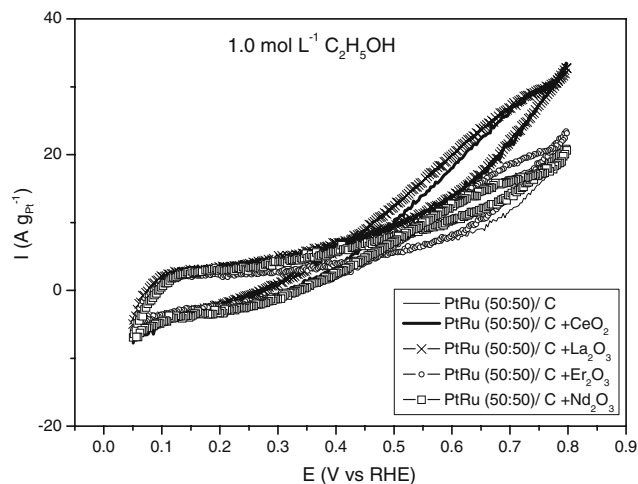


Fig. 3 Cyclic voltammograms of PtRu/C (50:50 catalyst metal; 100% C as support) and PtRu/C- CeO_2 , PtRu/C- La_2O_3 , PtRu/C- Nd_2O_3 , and PtRu/C- Er_2O_3 (50:50 catalyst metal; 85% C and 15% RE as support) in 1 mol L^{-1} ethanol solution in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ with a sweep rate of 10 mV s^{-1}

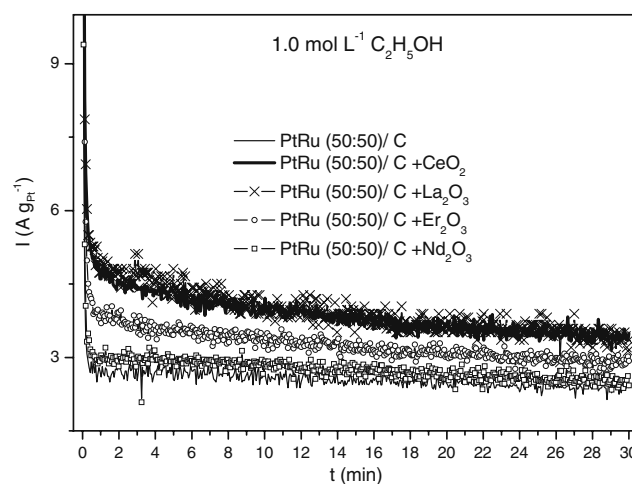


Fig. 4 Current-time curves at 0.5 V in 1 mol L^{-1} ethanol solution in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ for PtRu/C (50:50 catalyst metal; 100% C as support) and PtRu/C- CeO_2 , PtRu/C- La_2O_3 , PtRu/C- Nd_2O_3 , and PtRu/C- Er_2O_3 (50:50 catalyst metal; 85% C and 15% RE as support)

authors attributed the enhancement of activity to the bifunctional mechanism, where CeO_2 favors the formation of chemisorbed oxygen species and promotes the oxidation of adsorbed intermediate species on the surface of platinum.

The chronoamperometry experiments were carried out to examine the performance electrochemical and stability of the electrocatalysts. The PtRu/C (50:50 catalyst metal; 100% C as support) and PtRu/C- CeO_2 , PtRu/C- La_2O_3 , PtRu/C- Nd_2O_3 , and PtRu/C- Er_2O_3 (50:50 catalyst metal; 85% C and 15%

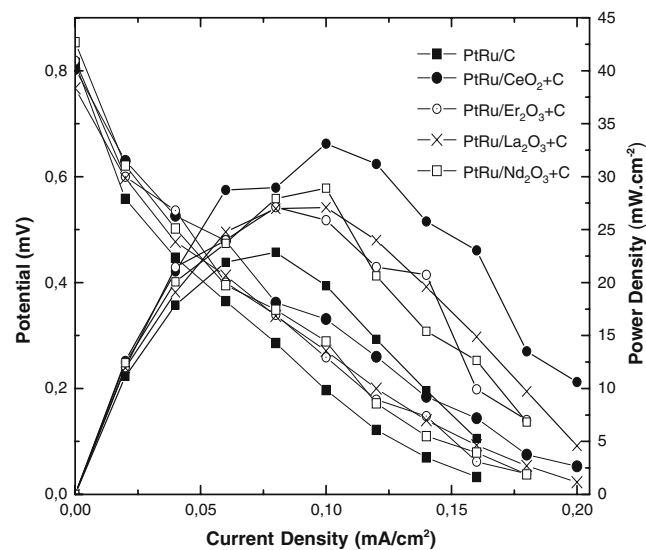


Fig. 5 I–V curves of a 5-cm^2 DEFC and the power density at 100°C using electrocatalysts anode with PtRu/C (50:50 catalyst metal; 100% C as support) and PtRu/C- CeO_2 , PtRu/C- La_2O_3 , PtRu/C- Nd_2O_3 , and PtRu/C- Er_2O_3 (50:50 catalyst metal; 85% C and 15% RE as support) (1 mg Pt cm^2 catalyst loading) and Pt/C E-TEK electrocatalysts cathode (1 mg Pt cm^2 catalyst loading, 20 wt.% catalyst on carbon), Nafion[®] 117 membrane, ethanol (2.0 mol L^{-1}), oxygen pressure (2 bar)

RE as support) chronoamperometry curves at 0.5 V are shown in Fig. 4. In all chronoamperometric curves, there is a sharp initial current drop in the first 1 min, and then the current values practically remain constant until 30 min. The current values obtained for PtRu/C-CeO₂, PtRu/C-Nd₂O₃, and PtRu/C-La₂O₃ were higher than those obtained for PtRu/C-Er₂O₃ and PtRu/C in agreement with CV results.

Figure 5 shows the performances of single fuel cell at 100 °C using PtRu/C, PtRu/C-CeO₂, PtRu/C-Er₂O₃, PtRu/C-La₂O₃, and PtRu/C-Nd₂O₃ as anode catalysts. The use of PtRu/C-RE electrocatalysts increased the cell performance with relation to PtRu/C, in agreement to the results obtained using electrochemical techniques. The maximum power density were the following: PtRu/C-CeO₂ electrocatalyst (33 mW cm⁻²)>PtRu/C-Nd₂O₃ (29 mW cm⁻²)>PtRu/C-La₂O₃ (27 mW cm⁻²)>PtRu/C-Er₂O₃ (26 mW cm⁻²)>PtRu/C electrocatalyst (23 mW cm⁻²). Probably, the release of oxygen species from the surface of RE oxides to Pt and/or Ru sites contributes to the oxidation of the intermediate species increasing the cell performance. The best result obtained using CeO₂ could be explained by its remarkable oxygen storage capability and catalytic properties [21–23].

Conclusion

The alcohol-reduction process showed to be an effective method for producing in a single-step active PtRu/C-RE electrocatalysts for ethanol oxidation. The XRD measurements showed peaks associated with the fcc structure characteristic of platinum. No peaks corresponding to ruthenium, CeO₂, Er₂O₃, La₂O₃, and Nd₂O₃ were observed. The PtRu/C-CeO₂ electrocatalyst exhibited higher performance for ethanol oxidation at room temperature than PtRu/C electrocatalyst. Tests at 100 °C on a single DEFC also confirm these results. Further work is now necessary to investigate the PtRu/C-RE electrocatalysts surface by different techniques and to elucidate the mechanism of ethanol electro-oxidation.

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