



Article The Promotional Effect of Rare Earth on Pt for Ethanol Electro-Oxidation and Its Application on DEFC

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Abstract: Bimetallic Pt_3Eu/C , Pt_3La/C , and Pt_3Ce/C electrocatalysts have been prepared, characterized, and tested for ethanol electro-oxidation (EEO). The materials were synthesized by chemical reduction with NaBH₄, rendering nanosized particles with actual compositions close to the nominals and no alloy formation. X-ray photoelectron spectroscopy (XPS) confirmed that the auxiliary rare-earth metals were present on the surface in oxide form. The electrochemical analyses in acid and alkaline EEO evidenced that, compared to Pt/C, the addition of rare earth metals in the form of oxides reduced the onset potential, increased the current density, and enhanced the stability. The results were fully confirmed in the DEFC single-cell measurements. Finally, the presence of rare earth metals in the oxidized form increased the percentage of acetic acid as the final product, making the electrocatalysts more selective and efficient than Pt/C, where acetaldehyde was the main product.

Keywords: DEFC; platinum; rare earth metals; ethanol electro-oxidation; product distribution

1. Introduction

The hydrogen economy is becoming closer to reality. Nevertheless, hydrogen presents some issues that can compromise its implementation, especially those related to its distribution, storage, and safety [1]. Liquid biofuels could play a complementary role in the hydrogen economy, acting indirectly as hydrogen (reforming) or energy (direct liquid fuel cells) sources, given their higher volumetric energy density and safer distribution and storage [2]. Ethanol occupies a prominent position as it is synthesized from sugarcane fermentation, and in countries such as the United States and Brazil, a well-established distribution network exists [3].

Direct Ethanol Fuel Cells (DEFCs) are one of the applications of ethanol as fuel. In DEFC, electricity can be directly produced from ethanol electro-oxidation (EEO) instead of direct combustion in engines [4,5]. DEFCs are generally applied in low-temperature solid polymer electrolyte fuel cells, limited to 90-130 °C due to the thermal limitations of the polymeric electrolyte membrane (Nafion[®], Dupont, Wilmington, DE, USA). The theoretical open circuit voltage of a DEFC, based on EEO and the oxygen reduction reaction, is 1.14 V [5]. The EEO is a complex process that involves ethanol dissociative adsorption, dehydrogenation, combination with neighboring OH_{ads} species, and C-C scission [6]. Noble metal platinum-based or palladium-based electrocatalysts, the latter in an alkaline medium, are the most widely used materials. Nevertheless, these noble metals undergo severe limitations due to surface poisoning with the carbonaceous species formed during the EEO (CH₃CO_{ads} and CO_{ads}), increasing the onset potential for the EEO (and thus



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). reducing the operating electrochemical window) and reducing the activity (limiting the current), leading to a reduced power output [7]. Moreover, the complete conversion of ethanol to carbon dioxide using the available 12 electrons is limited at low temperatures, forming acetaldehyde (2 electrons) and acetic acid (4 electrons) as the main EEO products, drastically reducing the faradic efficiency.

To improve the Pt (or Pd) noble metal activity towards EEO, these metals are combined with more labile auxiliary metal(s) to form bi-/tri- or even multimetallic materials. Focusing on Pt, with this approach, it is possible to supply the required oxygenated species to oxidize the adsorbed species formed onto the noble metal surface, thus refreshing the catalyst active sites (bifunctional mechanism), in addition to the modification of the electron filling of the Pt 5d band to alter the adsorption strength of the adsorbates formed during the EEO (electronic effect). In general, both mechanisms act together in multimetallic materials [8]. Previous studies have demonstrated that rare earth (RE) metals are very promising for promoting Pt EEO activity. Neto et al. [9] first applied RE metals to EEO by modifying Pt. They observed an increase in performance attributed to the bifunctional effect. The same research group prepared trimetallic materials based on the active PtSn and PtRu bimetallic materials, to which RE oxides (REO) were used as support (with carbon). The EEO activity and durability, as well as the single-cell DEFC, improved with this approach. Later, Corradini et al. [10,11] demonstrated that beyond the bifunctional mechanism, the presence of Pr_2O_3 in a PtPr/C electrocatalyst influenced the filling of the Pt 5d band (electronic effect). Corradini et al. [12] extended their work to La, Eu, and Ce, observing an increased CO tolerance and EEO activity. Finally, Santos et al. [13] prepared bimetallic Pt-RE (Ce, Sm, Ho, and Dy) alloys by thermal induction treatment under an inert atmosphere. The results displayed an enhancement of EEO activity with a smaller onset potential and a higher EEO maximum current density. In alkaline medium, several studies have also demonstrated the ability of rare-earth metals to promote Pt, Pd, or Ni EEO activity by the electronic (further boosted by the oxygen vacancies present in some REO) and bifunctional effects [14–21], extending the promotional effect of the REO to the whole range of pH.

Based on the previous promising studies showing the excellent synergistic properties of RE on Pt, this work proposes the application of three RE metals, La, Ce, and Eu. Additionally, Brazil is the third-largest worldwide reserve of these metals [22], with enormous potential for utilization. Co-deposited Pt:RE metals were prepared by chemical reduction with sodium borohydride. The materials were characterized by thermogravimetric analysis (TGA), X-ray diffractometry (XRD), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) to obtain basic structural information. Afterward, the prepared materials were electrochemically tested for EEO in acidic and alkaline media and a single-cell neutral and alkaline DEFC, with a final analysis of the oxidation products formed in both environments.

2. Results and Discussions

2.1. Physicochemical Characterization

Table 1 summarizes the main parameters that can be obtained from the TGA and EDS analyses. The metal wt.% and the Pt:RE atomic ratio can be inferred from these analyses. Additionally, Table 1 presents the labels used for the electrocatalysts. The calculated metal loadings are relatively close to the nominal ones, with an apparent systematic error of a slightly higher metal loading. One possible reason is the formation of metal oxides during the carbon combustion process. Regarding the Pt:RE metal ratio, the obtained values also agree with the nominal ones. This corroborates the successful deposition of the metals on the carbon support.

Catalyst	Label	Metal wt.%	Pt:RE Atomic Ratio (Nominal Value of 75:25)	Average Crystallite Size (nm)
Pt/C	Pt	22.5	-	4.6
Pt_3La/C	Pt3LaC	21.9	78:22	4.3
Pt ₃ Eu/C	Pt3EuC	21.9	77:23	5.2
Pt ₃ Ce/C	Pt3CeC	21.6	78:22	3.8

Table 1. Metal wt.% and Pt:RE metal atomic ratio of the prepared electrocatalysts.

Figure 1 shows the diffractograms of the prepared materials. The four electrocatalysts show the peaks associated with Pt (111), (200), (220), (311), and (222) at 40, 46, 67, 81, and 86 2 θ angles, respectively. It is also important to note the absence of peaks associated with any oxide phase. Given that there is no shift in the Pt diffraction peaks, we can hypothesize the deposition of the RE metals in the form of amorphous oxides. The average crystal sizes of the materials are also collected in Table 1. All the materials were deposited on the carbon support in the form of nanometric crystals.



Figure 1. Diffractograms of the different prepared catalysts (lines correspond to the diffraction peaks of Pt (111), (200), (220), (311), and (222) fcc crystal structures).

Figure 2 shows the corresponding TEM images of the four materials. All the micrographs confirm that the deposited catalyst particles are on the nanosized scale. The standard deviations (SD), estimated as a parameter to quantify the particle size dispersions, show relatively low values, indicative of a narrow distribution of the particle size distributions. Slightly higher values of the average particle size (D_{av}) and SD are observed for the bimetallic materials, especially Pt3EuC, where large particles and a less homogeneous distribution can be observed. Nonetheless, the micrographs confirm the deposition of the Pt nanoparticles in the range of a few nanometers, which is satisfactory for their application in DEFC.



Figure 2. TEM images of the four prepared catalysts and the average particle sizes (D_{av}) and the standard deviations (SD).

To complete the physicochemical characterization of the prepared catalysts, Figure 3 shows the XPS spectra of the corresponding materials, focusing on the Pt and RE metal spectra. Table 2 collects the quantification of the metal surface composition and the binding energies of the Pt 4f bands, along with the percentages of Pt metallic and oxidized species. As can be seen, all the bimetallic materials display a slight increase in the binding energy (BE) of the Pt 4f photoelectrons compared to PtC, indicating an electronic impact of the presence of the REO on the electronic environment of Pt. Platinum could transfer electrons through the Pt-REO interface, increasing the fraction of oxidized platinum and, consequently, the binding energy [23,24]. Such an effect strongly influences the adsorption energy of the different species during the EEO. The RE metals show the typical peaks of the oxide species, mainly La₂O₃ [25], Eu₂O₃ [26], and CeO₂ [27], as a result of the hydrolysis of the chlorides. Furthermore, the Ce and Eu 3D spectra show the presence of reduced species Ce(III) and Eu(II) in a minor proportion compared to the primary Ce(IV) and La(III). The presence of these species confirms that the Pt-Ce(IV) and Pt-Eu(III) interactions originated from the electron transfer of Pt to REO [28,29]. The presence of oxides is beneficial as they can participate in the EEO by providing oxygenated species (bifunctional mechanism) [30].



Figure 3. Cont.



Figure 3. XPS spectra of the different catalysts: (a) PtC, (b) Pt3LaC, (c) Pt3EuC, and (d) Pt3CeC.

Table 2. Atomic surface composition from the XPS results, binding energies of the Pt $4f_{7/2}$ bands, and the percentages of metallic and oxidized Pt species in parentheses.

Catalwat	At. % on the Nanoparticle Surface		Pt 4f _{7/2} XPS BE (% of Each Species in Parentheses)	
Catalyst	Pt	RE	Pt ⁰	Oxidized (II or IV) Pt
PtC	100		71.10 (61)	71.90 (39)
Pt3LaC	56.65	43.35	71.58 (46)	72.71 (54)
Pt3EuC	59.04	40.96	71.53 (51)	72.46 (49)
Pt3CeC	53.53	46.47	71.52 (50)	72.46 (50)

2.2. Electrochemical Measurements

2.2.1. Three-Electrode Glass Cell Results

Figures S1 and S2 collect the corresponding blank and CO stripping voltammetries for the different catalysts. These measurements allow estimating the electrochemically active surface area (EASA) used to normalize the EOR curves (EASA normalized curves) along with the mass of Pt (mass normalized curves). Figure 4 displays the EEO curves for H₂SO₄ and KOH electrolytes. The voltammograms show the positive effects of adding REO to platinum in the catalyst formulation. In an acid medium, the onset potential of the three bimetallic materials reduces from approx. 0.44 V to 0.3 V vs. reversible hydrogen electrode (RHE). Furthermore, the maximum current density also increases for the bimetallic materials, evidencing the improvement in the EEO by the electronic and bifunctional effects that the REOs exert on platinum. Among the three materials, the best performance is achieved with Pt3CeC. This could be explained by the presence of oxygen vacancies coming from the observed presence of Ce(IV) and Ce(III) simultaneously, which have been previously reported to be active for promoting Pt activity towards CO oxidation [31]. The same tendencies can be observed in an alkaline medium, corroborating the benefits of the REO on the Pt electrocatalyst. Figure S3 shows the results of the chronoamperometries, confirming the best performance of the Pt3CeC not only in terms of activity but also regarding long-term stability (less poisoned by the strongly adsorbed residues formed during the EEO). Nonetheless, future studies must address a crucial aspect of the bimetallic materials: the potential dissolution of the more liable RE metals/oxides.



Figure 4. EEO curves for the different electrocatalysts in 1 mol L^{-1} ethanol, (**a**) 0.5 mol L^{-1} H₂SO₄, and (**b**) 1 mol L^{-1} KOH (curves are normalized to the mass of Pt and the Pt EASA).

2.2.2. Single-Cell DEFC Tests

Figure 5 shows the fuel cell results for the DEFC operated with neutral (2 mol L^{-1} ethanol) and basified (2 mol L^{-1} ethanol + 4 mol L^{-1} KOH) fuels. As can be seen, regardless of the medium, the performance of the bimetallic materials is higher than that of PtC, corroborating the promotional effect of the auxiliary REO on Pt. In the neutral medium, the PtC open circuit voltage (OCV) is notably lower, which is consistent with the higher onset potential that PtC presents for EEO. Among the three bimetallic materials, Pt3CeC stands out due to its more intense electronic and bifunctional effects and the more robust oxygen vacancies in the cerium oxide. In the alkaline medium, the OCV is not so intensively affected by the addition of the REO. In alkaline medium, it is known that Pt presents a preoxidation peak due to the adsorption of OH⁻ on its surface at a lower potential than that of the formation of the platinum oxide layer [32]. Such a feature could explain the very close OCV of PtC and Pt-REO catalysts. However, over the polarization curves, the promotional effects of the RE become evident, allowing a lower poisoning of the Pt surface. As in the acid medium, Pt3CeC is the most active catalyst, achieving the highest current densities. The power density curves are presented in Figure S4. The results corroborate the tendencies observed in the polarization curves, with an increase in the maximum power density from 1.6 for PtC to 6.3 mW cm⁻² for Pt3CeC in the neutral medium. In the alkaline medium, the maximum power density increases from 1.8 for PtC to 4.7 mW cm⁻² for Pt3CeC. Thus, Pt3CeC emerges as the most active material in both acidic and alkaline mediums.



Figure 5. Polarization curves of the DEFC with different anode fuels (**a**) $2 \mod L^{-1}$ ethanol, (**b**) $2 \mod L^{-1}$ ethanol, and $4 \mod L^{-1}$ KOH.

2.3. Identification and Quantification of the Oxidation Products

The EEO product distribution is known to be affected by the catalyst composition [33,34]. Figure 6 presents the corresponding product selectivity in the neutral and alkaline mediums at different currents.



Figure 6. Products distribution of the DEFC when 2 mol L^{-1} ethanol is used as fuel at (**a**) 20 mA and (**b**) 40 mA; and the corresponding distributions when 2 mol L^{-1} ethanol and 4 mol L^{-1} KOH are used as fuel at (**c**) 20 mA, and (**d**) 40 mA.

As can be observed, CO_2 (or carbonate in an alkaline medium), the most desirable product to maximize the coulombic efficiency of the DEFC, is scarcely formed when the neutral fuel is fed to the cell and is absent in alkaline conditions. Moreover, adding the auxiliary RE metals further reduces the percentage of carbon dioxide and promotes the production of acetic acid instead of acetaldehyde compared to PtC. This result has already been observed in the literature for PtRu/C and PtSn/C electrocatalysts, in which most of the Ru and Sn were in the form of oxides. The large availability of oxygenated species surrounding the Pt active surfaces is responsible for favoring a more profound oxidation of the ethanol molecule to form acetic acid (oxidation of CH₃CO_{ads} with the neighboring OH_{ads} species to form CH₃COOH). Under these conditions, the formation of acetic acid is favored compared to C-C scission [34,35]. In the alkaline medium, hydroxyl anions that can adsorb onto the Pt surface can promote the significant formation of potassium acetate compared to acetaldehyde and inhibit the formation of potassium carbonate, further stimulated by the presence of the REO. In any case, contrary to the increase in activity observed by the addition of the RE in terms of electrochemical activity, the coulombic efficiency of the EEO becomes more limited when the RE metals are present in the catalyst formulation due to the promotion of the acetic acid route instead of the cleavage of the C-C bond in the ethanol molecule.

3. Materials and Methods

3.1. Chemicals

The following chemicals were used in the synthesis of the electrocatalysts: $H_2PtCl_6 \cdot 6H_2O$ (Pt precursor), LaCl₃, EuCl₃, and CeCl₃ as La, Eu, and Ce precursors, respectively, were purchased from Sigma-Aldrich (São Paulo, Brazil). NaBH₄, the reducing agent; acetaldehyde (ACS reagent, \geq 99.5%); ethyl acetate (suitable for HPLC, \geq 99.7%); and Nafion[®] 117 membranes (polymeric electrolyte) were also acquired from Sigma-Aldrich. The solvent 2-propanol (99.5%, ISO PA), acetic acid (GLACIAL UV/HPLC), and fuel ethanol (99.5%, ISO PA) were bought from Dinâmica (São Paulo, Brazil). The Nafion emulsion (5 wt.% in a mixture of aliphatic alcohols) was acquired from IonPower (New Castle, DE, USA).

3.2. Preparation of the Catalysts

The catalysts were prepared by chemical reduction in solution using the reducing agent NaBH₄. All the bimetallic materials presented a Pt/second metal atomic ratio of 3:1. The synthesis consisted of preparing 100 mg of catalysts with a total metal weight percentage of 20%. For the co-deposited bimetallic materials, the required metal precursor masses were dissolved in 100 mL of water, to which 80 mg of carbon black Vulcan XC-72R (Cabot Corp., Boston, MA, USA) were added. To facilitate the humectation of the carbon support, 1 mL of 2-propanol was added to the synthesis medium. The mixture was ultrasonicated for 30 min to guarantee the dispersion of all the chemicals. Next, an excess of NaBH₄ (mole ratio NaBH₄/metals of 5) was dissolved in 10 mL of a 0.01 mol L⁻¹ NaOH solution (to avoid the borohydride hydrolysis). The reducing agent was rapidly added to the metal precursors + carbon suspension, and the system was left for 24 h to complete the reduction. Once the synthesis time had elapsed, the prepared materials were filtered, washed thoroughly with deionized water, and dried for 4 h at 70 °C in an oven. As reference material, 20 wt.% Pt on carbon was also synthesized following the same procedure, except for the sole addition of the Pt precursor.

3.3. Structural and Morphological Characterization

To measure the metal loading, TGAs were applied to the prepared materials. A mass of 4 mg of the catalysts was transferred to an alumina pan. The samples were heated from 25 to 900 °C in synthetic air in a Shimadzu DTG-60H (Shimadzu Corp., Kyoto, Japan) at a heating rate of 10 °C min⁻¹. The Pt:RE atomic ratio was quantified by EDS in a scanning electron microscope Jeol JSM-6610 (Jeol Ltd., Tokyo, Japan). The crystallinity of the samples and the average crystallite size were measured by XRD in a Bruker D8 Focus diffractometer (Bruker Corp., Billerica, MA, USA), scanning from 2 θ angles from 5 to 80° at 0.5° min⁻¹ (step 0.05°), applying the Cu K_{α} radiation, 0.15406 nm. Transmission electron micrographs were obtained to calculate the particle size distribution in a microscope, the JEOL JEM-2100 (Jeol Ltd., Tokyo, Japan). Several images were obtained to estimate the average particle size (D_{av}) from the analysis of approximately 300 particles (n_i is the number of particles of size D_i) (Equation (1)).

$$D_{av} = \frac{\sum_{i} n_i D_i}{\sum_{i} n_i} \tag{1}$$

XPS spectra were recorded using a Physical Electronics (PHI) 5800-01 Spectrometer (Chanhassen, MN, USA). A monochromatic AlK_{α} X-ray source was used at a power of 350 W. Spectra were obtained with pass energies of 58.7 eV for elemental analysis and

11.75 eV to determine the oxidation states. The pressure in the analysis chamber of the spectrometer was 10^{-9} torr during measurements. After argon sputtering, the Ag $3d_{5/2}$ peak of an Ag foil was used to check the calibration of the binding energy scale. Quantitative evaluation of each peak was performed by dividing the integrated peak area by atomic sensitivity factors, which were calculated from the ionization cross-sections, the mean free electron escape depth, and the measured transmission functions of the spectrometer. XPS data were interpreted using the online library of oxidation states implemented in PHI MultiPak 6.1 software (Chanhassen, MN, USA, 1999) and the PHI Handbook of X-ray photoelectron spectroscopy.

3.4. Electrochemical Measurements

The electrochemical activity of the materials was initially evaluated in a three-electrode glass cell. The working electrode was prepared by dispersing 4 mg of the electrocatalysts in 1 mL of 2-propanol and adding 10 μ L of the Nafion emulsion, which acts as a polymeric binder to give adhesion to the deposited layer. This mixture was thoroughly sonicated, dropping 10 μ L onto a reticulated vitreous carbon electrode in a Teflon rod. The counterelectrode was platinized platinum gauze. The reference electrode in the acid medium was Ag/AgCl (KCl 3.5 mol L^{-1}), and Hg/HgO (KOH 1 mol L^{-1}) in the alkaline medium. Blank voltammetries were obtained in the supporting electrolytes, 0.5 mol L^{-1} H₂SO₄ and 1 mol L^{-1} KOH. EEO curves were also obtained by adding the required volume of ethanol to the supporting electrolyte to render a 1 mol L^{-1} alcohol solution. Moreover, COstripping experiments in the supporting electrolyte were carried out by initially polarizing the electrode at -0.15 V vs. Ag/AgCl in the acid medium and -0.876 V vs. Hg/HgO in the alkaline medium for 1 h. During this period, CO was bubbled for 20 min. In the sequence, CO is replaced by N_2 to remove the absorbed CO. Three consecutive voltamperometric cycles were applied to obtain the CO-stripping profiles. To assess the stability of the prepared electrocatalysts, a 12 h chronoamperometry was carried out at 0.726 V vs. RHE. This potential was chosen given that, according to Figure 4, the EEO is fully developed and, thus, the activity deactivation could be more visible. It is important to note that all the potentials presented in this work refer to the reversible hydrogen electrode. The potentiostat/galvanostat µAutolab TYPE III (Metrohm, Herisau, Switzerland) was used to perform the electrochemical measurements.

3.5. DEFC Experiments and EEO Products Quantification

Final DEFC single-cell experiments were carried out to test the cell performance and the effect of the RE addition to Pt under more realistic conditions. Diffusion electrodes were prepared by preparing a catalytic slurry composed of the required amount of catalyst (metal loading of 2 mg cm⁻² for an active area of 4 cm², from 20 wt.% metals on carbon for the anode; cathode Pt loading of 1 mg cm⁻² from 20 wt.% commercial Pt/C, Premetek, Cherry Hill, NJ, USA), Nafion emulsion as ionomer/binder (10 wt.% of the carbon mass present in the catalyst), and 1 mL of 2-propanol as solvent. This mixture rendered a thick slurry that was carefully paint-brushed on a carbon cloth (ZOLTEK[™] PX30 Fabric, PW03, Bridgeton, MO, USA). The diffusion electrodes were sandwiched between the Nafion[®] 117 membranes. Hot pressing was applied to assemble the membrane and electrodes at 130 °C and 3 tons for 3 min, obtaining the membrane electrode assembly (MEA).

The MEA was placed within a single-cell rig. The system consisted of two graphite monopolar plates with two parallel channels in a serpentine geometry. The end plate current collectors were fabricated in 316 stainless steel with perforations to place the heating rods. A drilled hole in the graphite plate was used to insert a K-thermocouple connected to a temperature controller (N1020, Novus Automation Inc., Crystal Lake, IL, USA). For the impulsion of the fuel solution, a peristaltic pump (Exatta Bombas, Palhoça, Brazil) was used, whose flow rates were previously calibrated. The oxygen flow was controlled with a flow meter RMS-11 (DIGIFLOW Medição e Controle de Fluídos Ltd.a, São Paulo, Brazil), fixing a value of 30 mL min⁻¹. More details can be found elsewhere [36].

The DEFC experiments were carried out at 70 °C, feeding a 2 mol L⁻¹ ethanol solution (neutral fuel) or 2 mol L^{-1} ethanol and 4 mol L^{-1} KOH (alkaline fuel). The oxidation products were identified and quantified by high-performance liquid chromatography (HPLC, PerkinElmer, Flexar model, Waltham, MA, USA), using a Polypore-H column (PerkinElmer) as stationary phase and a 6.25 mmol L^{-1} H₂SO₄ as the mobile phase. The applied flow rate was 0.5 mL min⁻¹. The UV-Vis detector identified the products at 190 nm. Analytical curves with ethanol, acetaldehyde, acetic acid, and ethyl acetate were prepared and used to quantify the concentrations of each product. This latter analysis was carried out by polarizing the cell galvanostatically at 20 and 40 mA for 1 h. Once this time had elapsed, a product sample was injected into the HPLC. Carbon dioxide was measured by mass spectrometry (MS, Dymaxion MS, Ametek, Berwyn, PA, USA) by dragging the gases accumulated in the fuel reservoir with N_2 . This reservoir was maintained in an ice bath to minimize the dragging of ethanol and acetaldehyde. The fuel cell exhaust from the alkaline fuel cell was poured into 4 mol L^{-1} H₂SO₄ to convert carbonate to CO₂. The m/z ratios that followed were 22 and 44, typical signals of CO₂. A previous calibration was carried out with CO₂ and N₂ mixtures of different CO₂ contents.

4. Conclusions

The addition of the RE metals La, Eu, and Ce to Pt to form bimetallic materials has proven to promote the electrochemical performance of platinum in the EEO reaction. Despite their deposition in the form of nanosized oxides, they exert an electronic effect on Pt and provide the oxidized species required for the EEO, rendering a notable increase in the DEFC's performance in terms of increasing the current and power densities. Finally, their presence also impacts the distribution of the oxidation products, favoring the formation of acetic acid as a counterpoint to the increase in electroactivity and limiting the coulombic efficiency as the C-C scission is disfavored.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13061011/s1, Figure S1. Blank CV of the electrocatalysts in (a) 0.5 mol L^{-1} H₂SO₄ and (b) 1 mol L^{-1} KOH; Figure S2. Blank CV of the electrocatalysts in (a) 0.5 mol L^{-1} H₂SO₄ and (b) 1 mol L^{-1} KOH; Table S1. Onset potential and EASA extracted from the CO stripping experiments; Figure S3. Ethanol electro-oxidation curves for the different electrocatalysts in 1 mol L^{-1} ethanol, (a) 0.5 mol L^{-1} H₂SO₄, and (b) 1 mol L^{-1} KOH; Table S1. Onset potential and EASA extracted from the CO stripping experiments; Figure S3. Ethanol electro-oxidation curves for the different electrocatalysts in 1 mol L^{-1} ethanol, (a) 0.5 mol L^{-1} H₂SO₄, and (b) 1 mol L^{-1} KOH (curves are normalized to the mass of Pt and Pt EASA); Figure S4. Power density curves of the DEFC with different anode fuels (a) 1 mol L^{-1} ethanol, (b) 1 mol L^{-1} KOH [37–40].

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