

Enhanced Activity of PtRu/85%C+15% Rare Earth for Methanol Oxidation in Acidic Medium

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Pt/C, PtRu/C, PtRu/C-Er₂O₃, PtRu/C-CeO₂, PtRu/C-La₂O₃ and PtRu/C-Nd₂O₃ 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, 85% Vulcan XC72 + 15% rare earth (RE) as support. The electro-oxidation of methanol was studied by cyclic voltammetry and chronoamperometry at room temperature. The Pt:Ru atomic ratios obtained by EDAX were very similar to the nominal ones and from XRD measurements it was observed a broad peak at about 25° was associated with the Vulcan XC72 support material and others peaks at approximately 2θ=40°, 47°, 67°, and 82°, which are associated with the (111), (200), (220), and (311) planes, respectively of the face-centered cubic (fcc) structure. No peaks corresponding to a metallic ruthenium, ruthenium oxide phase, CeO₂, Er₂O₃, La₂O₃ or Nd₂O₃ were observed. TEM micrographs of all electrocatalysts also showed a good distribution of the particles on the carbon support and the average particle sizes were in the range of 2.0–3.0 nm. PtRu/CeO₂-C and PtRu/La₂O₃-C electrocatalysts had a higher performance for methanol oxidation compared to others electrocatalysts prepared. The final current values after holding the cell potential at 0.5 V versus RHE for 30 min were the following: PtRu/CeO₂-C > PtRu/La₂O₃-C > PtRu/Er₂O₃-C ≈ PtRu/C > PtSn/Nd₂O₃-C > Pt/C.

Keywords: PtRu/85%C+15% Rare Earth, methanol electro-oxidation, acidic medium, electrocatalysts, fuel cell

1. INTRODUCTION

Direct methanol fuel cell (DMFC) are attractive as power sources for mobile, stationary and portable applications, because the use of liquid fuels simplifies the fuel delivery system compared to

hydrogen-fed fuel cells, which need a reforming system or have problems of hydrogen storage [1-2]. Methanol also has been considered the most promising fuel, because it is more efficiently oxidized than other alcohols. For methanol oxidation a platinum electrocatalyst (Pt/C) is commonly used as anode in low temperature fuel cells, however, the Pt/C is not an efficient electrocatalyst for the direct methanol fuel cells, because it is rapidly poisoned by strongly adsorbed species coming from the dissociative adsorption of methanol. [3].

In recent years, it is found that certain metal oxides, such as CeO₂, RuO₂ or SnO₂, can enhance the catalytic activity for methanol or ethanol electro-oxidation through synergetic interaction with Pt [4-6]. The Pt sites act as adsorption and dehydrogenation centers for methanol, while the ruthenium oxides sites provide oxygen-containing species at lower potentials than those on a pure Pt surface [6].

It has found that PtRu alloys are the most effective bimetallic Pt-based catalysts for methanol oxidation, but the Ru metal can be dissolved from the PtRu electrocatalyst surface under electrochemical conditions, which results in the performance degradation of DMFC [7], consequently yet it is necessary to develop new and more efficient PtRu/C electrocatalysts [8]. It has been described that the addition of a third element to PtRu/C electrocatalyst could increase its activity for methanol oxidation [8].

Recently, Ribeiro et al [9] showed that the PtRuNi/C electrocatalyst prepared with OH⁻/metals = 6 had superior performance for methanol oxidation at room temperature compared to commercial PtRu/C electrocatalyst.

Huang et al. [10] also prepared PtRuMe (Me = Fe, Co, Ni) electrocatalysts dispersed on multi-walled carbon nanotubes (MWCNTs) by ultrasonic-assisted chemical reduction and the electrochemical measurements showed that the addition of Me to PtRu enhanced the electrocatalytic properties for methanol oxidation. PtRuNi electrocatalyst also showed the highest catalytic activity and stability in comparison with others electrocatalysts prepared.

Another alternative is use Rare earth (RE) materials, because Rare earth oxides exhibit a number of characteristics that make them interesting for catalytic studies, as the electronic effect [7]. Moreover, the oxides rare earth also are capable of adsorbing large quantities of OH⁻ species, which are involved in the oxidation/reduction mechanisms between the different possible oxidation states of the metal oxides. The oxygen containing species usually is beneficial to the oxidation of some poisoning intermediates.

Recently, Neto et al [11-13] showed that the PtEr/C, PtTb/C, PtLa/C, PtDy/C and PtNd/C electrocatalysts prepared by alcohol reduction process had superior performance for methanol electro-oxidation at room temperature compared to Pt/C, on the other hand, the performance of PtRu/C electrocatalyst was superior to Pt-RareEarth/C prepared, consequently could be more interesting the addition of rare earth elements to PtRu electrocatalyst.

In this context, the aim of this work was to prepare PtRu/C, PtRu/Er₂O₃-C, PtRu/CeO₂-C, PtRu/La₂O₃-C and PtRu/Nd₂O₃-C electrocatalysts by an alcohol-reduction process substituting part of the carbon support by rare earth oxides.

The obtained materials were tested for methanol oxidation using electrochemical techniques (voltammetry and chronoamperometry).

2. EXPERIMENTAL

PtRu/C, PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃ and PtRu/C-Er₂O₃ 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, 85% Vulcan XC72 + 15% RE (Aldrich) as support. The atomic composition of the PRu/C and PtRu/C –earth rare electrocatalysts prepared using alcohol reduction process was chosen to be 50:50, the most active composition for the methanol or ethanol electro-oxidation [14].

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 ultrasonic bath and were refluxed for 3 h under open atmosphere. The mixtures were filtered and the solid was washed with water and dried at 70 °C for 2h.

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

XRD analyses were performed using a Rigaku diffractometer model Miniflex II with a CuK 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 2s/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 of 150 nanoparticles from micrographs using Image Tool Software.

Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique [14]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing 3 drops of a 6% solution polytetrafluoroethylene (PTFE) suspension. The resulting mixture was treated in an ultrasound bath for 10 min, filtered and transferred to the cavity (0.30 mm deep and 0.47 cm² area) of the working electrode. In cyclic voltammetry and chronoamperometry experiments the current values (*I*) were expressed in amperes and were normalized per gram of platinum (A g Pt⁻¹). 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 Pt plate.

Cyclic voltammetry experiments were performed in 0.5 mol L⁻¹ H₂SO₄ solution saturated with N₂ using a Microquímica (model MQPG01, Brazil) potentiostat/galvanostat in presence and absence of 1.0 mol L⁻¹ of methanol, while that the chronoamperometry curves of the Pt/C, PtRu/C, PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃ and PtRu/C-Er₂O₃ electrocatalysts were performed holding the cell potential at 0.5 V vs RHE in 0.5 mol L⁻¹ H₂SO₄ solution containing 1.0 mol L⁻¹ CH₃OH at room temperature.

3. RESULTS AND DISCUSSION

As already published for PtRu/C, PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃ and PtRu/C-Er₂O₃ electrocatalysts [8], the Pt:Ru atomic ratios obtained by EDAX were very similar to the nominal ones and from XRD measurements it was observed a broad peak at about 25° was associated with the

Vulcan XC72 support material and others peaks at approximately $2\theta=40^\circ$, 47° , 67° , and 82° , 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. TEM micrographs of all electrocatalysts prepared also 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 [8].

Figure 1 shows the cyclic voltammograms (CV) in the absence of methanol of Pt/C, PtRu/C, PtRu/C- CeO_2 , PtRu/C- La_2O_3 , PtRu/C- Nd_2O_3 and PtRu/C- Er_2O_3 electrocatalysts.

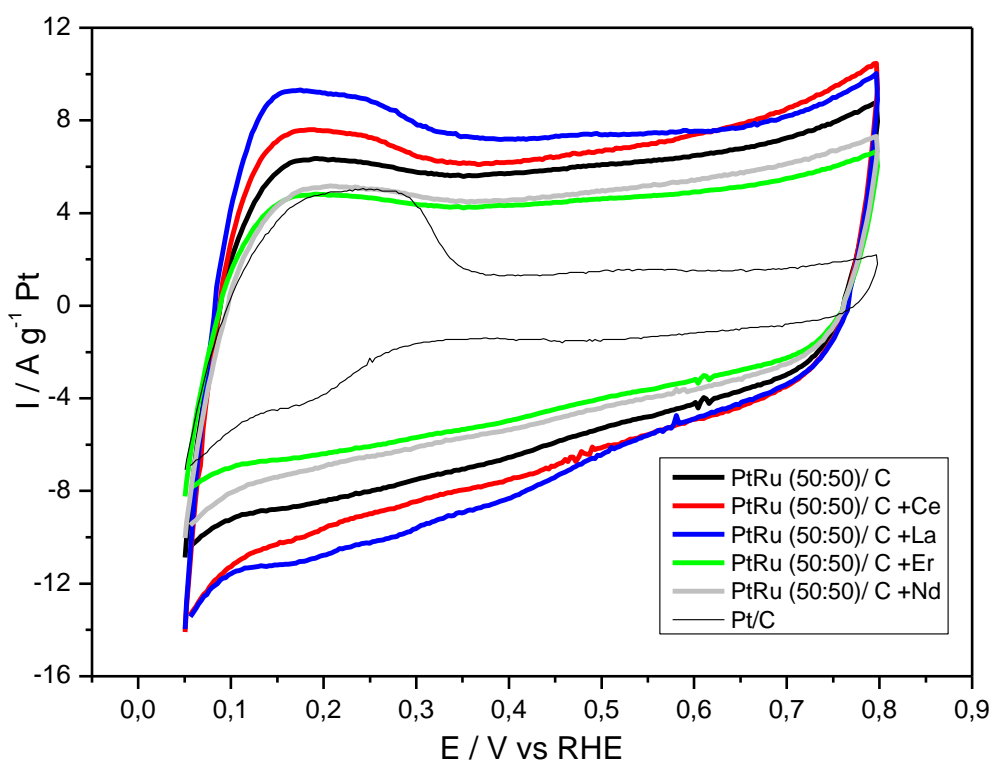


Figure 1. Cyclic voltammograms of Pt/C, PtRu/C, PtRu/C- CeO_2 , PtRu/C- La_2O_3 , PtRu/C- Nd_2O_3 and PtRu/C- Er_2O_3 electrocatalysts in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, sweep rate of 10 mV s^{-1} .

The cyclic voltammogram for all PtRu electrocatalyst do not show a well-defined hydrogen adsorption-desorption region (0.05–0.4 V) in comparison with Pt/C electrocatalysts. It was observed an increase in the current values in the double layer (0.4–0.8 V), which may be attributed to the formation of oxide species [15]. The currents values in the double layer region were high for PtRu/C- La_2O_3 and PtRu/C- CeO_2 indicating more formation of oxide species. The negative scan also showed an increase in the currents in the double layer at about 0.6 V that could be associated with the reduction of oxide species presents in the electrocatalyst.

PtRu/C- La_2O_3 and PtRu/C- CeO_2 electrocatalyst had a more defined hydrogen adsorption-desorption region than PtRu/C and others electrocatalysts prepared by alcohol reduction process implying that the true active areas of the electrodes are largest. The charge associated to the double

layer for PtRu/C-La₂O₃ and PtRu/C-CeO₂ was similar, this could imply that the true active areas of the electrodes are nearly the same.

Figure 2 shows the CV of PtRu/C, PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃ and PtRu/C-Er₂O₃ 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 methanol and 0.5 mol L⁻¹ H₂SO₄.

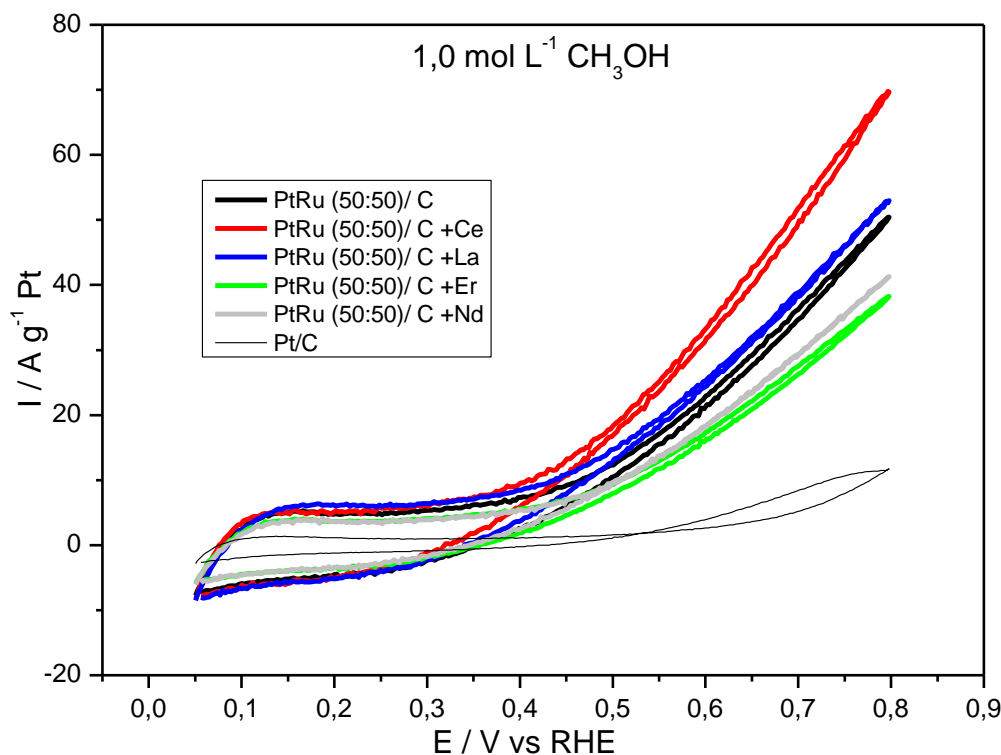


Figure 2. Cyclic voltammograms of Pt/C, PtRu/C, PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃ and PtRu/C-Er₂O₃ in 1 mol L⁻¹ methanol solution in 0.5 mol L⁻¹ H₂SO₄ with a sweep rate of 10 mV s⁻¹.

The cyclic voltammograms of the all electrocatalysts showed the hydrogen desorption/sorption region was significantly suppressed in the presence of methanol in the solution in comparison with absence of the methanol. The electro-oxidation of methanol started at approximately 0.35 V for PtRu/C-CeO₂, PtRu/C-La₂O₃ and PtRu/C, for PtRu/C-Er₂O₃ and PtRu/C-Nd₂O₃ the electro-oxidation of ethanol started at approximately 0.40 V, while that for Pt/C the electro-oxidation of methanol started at approximately 0.60 V. Thus results confirmed that the Pt is not an efficient electrocatalyst for the direct methanol fuel cells.

PtRu/C-CeO₂ and PtRu/C-La₂O₃ 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 [8] also showed the enhancement of activity for ethanol electro-oxidation resulting from the addition of CeO₂ and La₂O₃ to platinum ruthenium electrocatalysts. The best activity of PtRu/C-CeO₂ and PtRu/C-La₂O₃ in comparison with Pt/C and PtRu/C could be attributed to the

bifunctional mechanism, where CeO_2 or La_2O_3 favor the formation of chemisorbed oxygen species and promotes the oxidation of adsorbed intermediate species on the surface of platinum or platinum-ruthenium.

In the potential range of interest for a direct methanol fuel cell (0.3 to 0.6 V), the current values of PtRu/C- La_2O_3 and PtRu/C- CeO_2 were higher than Pt/C and PtRu/C. This result confirmed that the addition of rare earth to PtRu/C was effectively improved its catalytic activity for methanol electro oxidation.

The chronoamperometry experiments for methanol oxidation using the Pt/C, PtRu/C, PtRu/C- CeO_2 , PtRu/C- La_2O_3 , PtRu/C- Nd_2O_3 and PtRu/C- Er_2O_3 were carried out to examine the electrochemical activity and stability of the electrocatalysts (Fig. 3). 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.

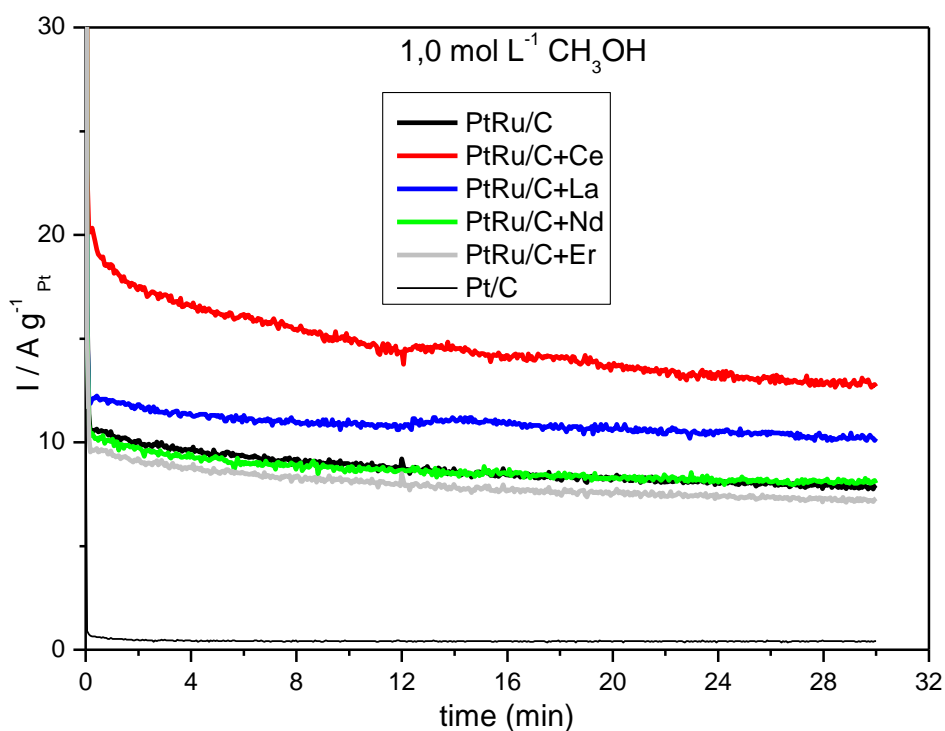


Figure 3. Current-time curves at 0.5 V in 1 mol L^{-1} methanol solution in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ for PtRu/C- Er_2O_3 and PtRu/C- CeO_2 , PtRu/C- La_2O_3 , PtRu/C- Nd_2O_3 , Pt/C and PtRu/C.

In all chronoamperometric curves, there is a sharp initial current drop in the first 2 min followed by a slower decay up to 12 min, after the current values practically remain constant until 30 min. The current values obtained for PtRu/C- CeO_2 and PtRu/C- La_2O_3 were higher than those obtained for PtRu/C- Nd_2O_3 , PtRu/C and PtRu/C- Er_2O_3 . The Pt/C also showed smaller current values in comparison with all others electrocatalysts prepared in agreement with CV results.

In accordance, Neto et al [8] also observed that the current values obtained for PtRu/C- CeO_2 in ethanol oxidation were higher than those obtained for PtRu/C. These authors concluded that the release

of oxygen species from the surface of RE oxides to Pt and/ or Ru sites contributes to the oxidation of the intermediate adsorbed increasing the cell performance.

The final current values at 30 min during chronoamperometry studies are shown in Fig. 4 for Pt/C, PtRu/C, PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃ and PtRu/C-Er₂O₃ electrocatalysts.

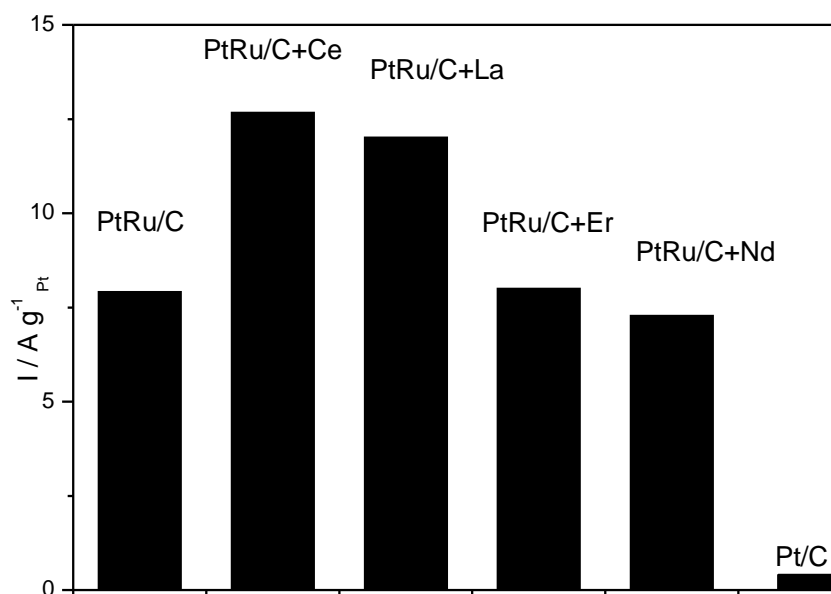


Figure 4. Current density values at 1800 s during chronoamperometry experiments for Pt/C, PtRu/C, PtRu/C-CeO₂, PtRu/C-La₂O₃, PtRu/C-Nd₂O₃ and PtRu/C-Er₂O₃ electrocatalysts.

The final current values after holding the cell potential at 0.5 V versus RHE for 30 min were the following: PtRu/C-CeO₂ > PtRu/C-La₂O₃-C > PtRu/C-Er₂O₃ ≈ PtRu/C > PtSn/C-Nd₂O₃ > Pt/C. The superior activity for methanol oxidation of PtRu/C-CeO₂ and PtRu/C-La₂O₃ compared to Pt/C or PtRu/C electrocatalyst probably could be attributed to the bi-functional mechanism, where Pt acts on methanol adsorption and dissociation and the ruthenium or Rare Earths provide oxygenated species at lower potentials. The best result obtained using CeO₂ could be explained by its remarkable oxygen storage capability and catalytic properties removal of adsorbed CO [16-18].

On other hand, An et al [7] showed that the current density measured at different catalyst by holding potential at 0.5 V for 1800 was ranked as an order of PtRuEu/C > PtRuEr/C > PtRuY/C > PtRuSm/C > PtRuLa/C > PtRu/C > PtRuGd/C. This result also confirmed that the addition of rare earth to PtRu/C has effectively improved its catalytic activity for methanol electro oxidation.

4. CONCLUSIONS

The alcohol-reduction process showed to be an effective method for producing in a single-step active PtRu/C-RE electrocatalysts for methanol oxidation. The PtRu/C-CeO₂ electrocatalyst exhibited

higher performance for methanol oxidation at room temperature in comparison with others electrocatalysts prepared. The best result obtained using CeO₂ could be explained by its remarkable oxygen storage capability and catalytic properties removal of adsorbed CO. Further work is now necessary to investigate the PtRu/C-RE electrocatalysts surface by different techniques. The results obtained in this manuscript are of importance for DMFC application.

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