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Synthesis and Characterization of Ru Enriched Pt-Ru Nanostructured Catalyst Prepared by Carbonyl-metal Complex Reduction for DMFC Redox Reactions

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Abstract: *Nanostructured Pt-Ru/C was synthesized by reducing the carbonyl-metal complex precursors. A modified two-step synthesis from conventional carbonyl metal reduction process was used for obtaining highly enriched Ru catalytic nanoparticles distributed onto normal carbon Vulcan. Structural characteristics of the synthesized catalysts were analyzed by transmission electron microscopy. A particle size distribution of 1.57 ± 0.09 nm was obtained for the synthesized catalyst. The chemical composition analysis showed Ru enriched Pt-Ru clusters deposited on Vulcan. The electrochemical characterization showed adequate catalytic properties to promote redox reactions in a direct methanol fuel cell environment.*

Keywords: Pt-Ru nanoparticles, DMFC, methanol oxidation, oxygen reduction, carbonyl.

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) have important characteristics as energy suppliers for mobile and electronic applications, and are considered as good alternative to lithium ion batteries [1]. The performance of DMFC requires the use of methanol and oxygen as reactants to carry out anodic and cathodic reactions to produce electrical power, CO_2 and water. Nevertheless, the use of methanol can cause catalytic losses in the anode of the fuel cell. Platinum has been the mostly used catalyst for anodic reactions, but it is easily poisoned because of CO adsorption on the surface of the Pt based anodic catalyst. The incorporation of a second noble metal, Ru, in the matrix of Pt catalyst, has aided to remove the adsorbed CO from the surface of the catalytic material [2,3]. Furthermore, trimetallic alloys have recently been investigated for alcohol oxidation fuel cell applications, but in all cases the basic material of the catalysts is Pt-Ru. Examples of these alloys are PtRuNi [4], PtRuFe [5], PtRuCo [6,7], and PtRuW [8]. These complex catalysts have shown adequate performance for oxiding methanol and the most important is the significant reduction in the amount of Pt used to catalyze redox reactions in a DMFC. The choice and preparation of anodic catalysts are necessary conditions to develop a good performance of DMFCs.

Nowadays, Pt-Ru supported on carbon is the most promising catalytic material for anodic reactions in DMFCs [9]. There are several experimental techniques to synthesize Pt-Ru supported on carbon or in colloidal nanoparticles showing high surface area. They can be prepared by co-precipitation [10], absorbing alloy colloids [11], and organometallic chemistry techniques [12].

The electroactivity of the synthesized catalysts for promoting redox reactions in a DMFC, is a function of the preparation conditions and the experimental procedures used for obtaining the supported catalysts. In this work we proposed a modified method based in a two-step synthesis of carbonyl-metal complex for obtaining nanostructures dispersed on the surface of carbon Vulcan, with the possibility to deposit one-type enriched catalyst. In this case Ru enriched Pt-Ru nanostructured catalyst was synthesized by carbonyl-metal complex reduction. The synthesized catalyst was structural, compositional and electrochemically characterized to investigate its nature and kinetic properties to perform redox reactions in DMFC environment.

2. EXPERIMENTAL DETAILS

Nanostructured Pt-Ru based bimetallic catalyst supported on carbon Vulcan XC-72R (Pt-Ru/C) was synthesized by carbonyl-metal complex reduction method. Nanostructured Pt-Ru/C was

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formed in a two-step synthesis method for obtaining good quality catalyst for methanol oxidation in DMFC applications.

2.1. Preparation of Pt Carbonyl Complex $[Pt(CO)_2]_x$

The oxidation reaction of the Pt precursor was carried out in aqueous solution using hydrated chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$), 99.9% purity Aldrich, highly hygroscopic and light-sensible. 520 mg of this active reagent was dissolved in 52 ml deionized water (18 MΩ Millipore^{TM}) in an Erlenmeyer Bulb. The solvated metallic salt was oxidized by bubbling carbon monoxide of 99.5% purity for 27 h and a magnetic stirring (550 rpm) was applied during the process. The experiment was performed at room temperature.

The carbonization process occurring in the Pt based salt by CO injection allowed the formation of the Pt carbonylic complex in a simple step. The carbonization reaction for obtaining Pt carbonylic complex is:

$$\begin{aligned}&[PtCl_6]^{-2} \longrightarrow [Pt(CO)Cl_3]^{-} \longrightarrow [Pt_3(CO)_6]_{\approx 10}^{-2} \\ &\longrightarrow [Pt_3(CO)_6]_6^{-2} \longrightarrow [Pt_3(CO)_6]_5^{-2}\end{aligned} \qquad (1)$$

In eq. (1), there is an insoluble anion, n=10, and it is reduced to soluble anion, n=6, and more simple anions by chemical reduction reaction (n tends to 1).

There was a change in the color of the solution, at the initial stage, the color was bright yellow, at the end of the process, the solution was black when the reduction reactions were carried out, indicating the formation of the Pt-carbonyl complex precursor, $[Pt(CO)_2]_x$. The solution was filtered using whatman #1 filter paper and the Pt-carbonyl precipitate was retrieved and maintained in an open vessel at room temperature. The reaction yield of this process is about 40% due to the chemical composition of the chloroplatinic acid. The precipitate was dried in carbon monoxide atmosphere using a sealed flask for 48 hours using a mechanical pump for removing the humidity from the sample. The dried Pt based carbonyl is a highly hygroscopic material. It was the synthesized precursor used in the preparation of nanostructured Pt-Ru supported on Vulcan. The Ru-carbonyl precursor $[Ru_3(CO)_{12}]$ high purity (99%) was obtained commercially from Aldrich Chemicals.

2.2. Preparation of nanostructured Pt-Ru supported on Vulcan

Pt-Ru based electrocatalyst for direct methanol fuel cell applications was synthesized from the Pt and Ru precursors previously discussed in this work. Pt-Ru/C nanoparticles were prepared in a round bottom flask by dissolving 198.5 mg of Pt-carbonyl, 168.8 mg of Ru-carbonyl and 234.45 mg of carbon Vulcan XC72R in 235 mL of o-xylene (95% purity, Spectrum chemical) as solvent. At the end, the Pt-Ru/C nanoparticles were synthesized by thermal decomposition reaction of the solution in a reflux system by heating at 140 Celsius using a mechanical stirring at 870 rpm for 27 hours. The corresponding reaction for obtaining nanostructured Pt-Ru catalyst supported on carbon Vulcan from the Pt and Ru precursors is shown in equation 2.

The recovering of solvent from the synthesis of nanostructured Pt-Ru/C was carried out in a rotating evaporator Buchi water-bath Model B-480 at 120 rpm and 140 Celsius for at least 5 hours until the supported catalyst was completely dried. At the end, the catalyst was heated at 150 Celsius in a tubular furnace for a period of 2 hours in a nitrogen atmosphere just to make sure the complete removal of solvent from the synthesized Pt-Ru/C. The synthesized catalyst showed a visual presentation as a very fine and opaque black powder.

Microstructural characteristics of the synthesized catalysts reported in this work were analyzed by transmission electron microscopy. Samples of Pt-Ru/C were prepared by ultrasonic dispersion of the catalyst in 2-propanol, a droplet of about 2 mL was deposited on a copper grid covered with amorphous carbon.

The electrochemical characterization of nanostructured Pt-Ru/C was carried out in a three compartment cell. The working electrode was formed with 1 mg of the catalyst mixed with 10 µl of Nafion solution (in 5% of aliphatic alcohols) and diluted in isopropanol in an ultrasonic bath. From the resulting ink, 5µl was deposited as a thin film on a graphite rotating disk electrode (RDE) with a cross-sectional area of 0.16 cm^2.

3. RESULTS

Pt-Ru/C synthesized by carbonyl-metal complex reduction was characterized by low and high resolution electron microscopy to analyze the nanostructured nature of the material. It is shown in figure 1 a typical TEM image of the synthesized Pt-Ru containing a well dispersion of nanoparticles without the presence of solvent that can affect the electrocatalytic activity of the nanoparticles, nevertheless it is possible to suggest the formation of nanoclusters due principally to the long exposure time of the precursors during the reduction time of active species as well as the annealing process. The sample was homogeneous in quasi-spherical formation with a particle size distribution of 1.57 ± 0.09 nm, and the particle mean size was in the range of 0.5 to 3.5 nm and according to the synthesis method it was possible to prepare Pt-Ru nanoparticles of around 2 nm with the best characteristics for methanol oxidation reaction.

The Pt-Ru based catalyst was characterized by Z-contrast mapping in a JEOL JEM2010F STEM/TEM for analyzing the compositional chemical elements of the sample

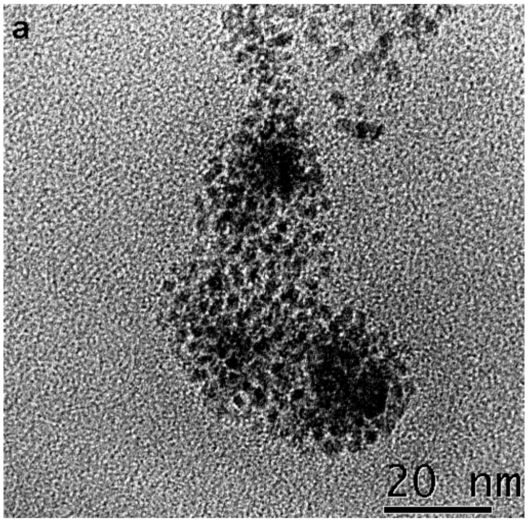

Figure 1. TEM image of a sample of synthesized and annealed Pt-Ru/C catalyst for methanol oxidation reaction.

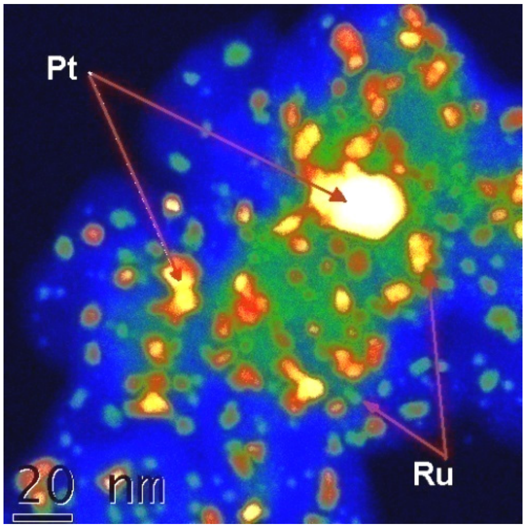

Figure 2. Chemical mapping by Z-Contrast image of highly Ru enriched Pt-Ru nanoparticles supported on Vulcan carbón XC 72R, Pt (yellow brightness), Ru (green).

Fig. 2 shows a typical image of the analysis by Z-contrast where it is possible to observe the formation of core-shells, where Ru (green spots), in the form of shells, is covering the Pt (yellow spots), the principal catalytic material in this system. Pt is placed in well defined core positions, formed by nanoclusters, and the Ru chemical element is placed surrounding the zones where Pt is located. It is also observed that the excess of Ru is located in a homogeneous spatial zone forming, in general, a continuous nanoparticle layer. The formation of this Ru layer, or in other words, the formation of Ru enriched Pt-Ru catalyst can have direct effect on the long-life cycling performance of the catalyst during the methanol oxidization reaction, acting like reaction precursor for splitting water molecules close to Pt-Ru nanoparticles. The complete water oxidation in the nearest zone of Pt-Ru avoids the poisoning of the principal catalytic material by the presence of CO, when it is formed in intermediate reactions from CH_3OH to CO_2 in a DMFC. This suggestion was based on the electrochemical studies performed in this work.

The synthesis method based on carbonyl-metal complex reduction of active species produces nanoparticles with good structural and electrochemical characteristics because of the very long reduction time needed to form nanoparticles, which allows the complete interaction of active species and the reduction process can be carried out to obtain nanoparticles of controlled particle size. By controlling particle size distribution it is possible to design electrocatalysts for a specific electrochemical application. In the case of methanol oxidation, it is considered that the particle size of the nanostructured catalysts should be in the range of 2 to 4 nm for the best results to oxide methanol [13]. It is possible to obtain a good control in particle size distribution of Pt-Ru/C based catalyst by controlling the synthesis time and precursor concentrations by using the synthesis method discussed in this work.

The composition of the Ru enriched Pt-Ru catalyst was analyzed by identifying the characteristic planes in a well defined nanoparticle from an HREM image of the sample (figure 3). The nanoparticle showed a quasi-spherical morphology and the two metallic phases (Pt and Ru) were observed. Spherical or quasi-spherical nanoparticles are the result of the synthesis method used for obtaining the nanostructured catalyst; in this case, the carbonyl-metal complex reduction process. The structural composition of the catalyst was carried out by measuring the interplanar distances of the nanoparticles using GATAN Digital Micrograph software.

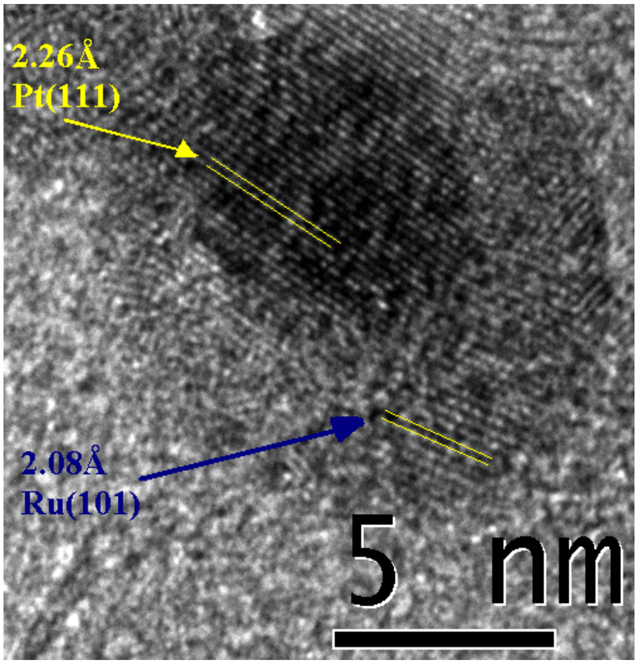

Figure 3. Identification of Pt and Ru phases in HREM image of Pt-Ru/C nanoparticles synthesized by carbonyl-metal complex reduction process.

Figure 3 shows a typical nanoparticle and its identified structures were Ru surrounding Pt nanoparticles was found. A very active fcc plane Pt(111) for promoting oxidation reactions was obtained at 2.26 Å interplanar distance. hcp plane Ru(101) was calculated at 2.08 Å interplanar distance in the vicinity of the Pt nanoparticle. It is possible to assume the formation of Pt-Ru bimetallic nanoparticles. It is not easy to establish a criterion to prove the formation of Pt-Ru bimetallic nanoparticles due to the similar values in interplanar distances between Pt and Ru, but that assumption could be reinforced by analyzing the chemical composition of the sample and its performance to promote redox reactions for direct methanol fuel cell applications.

The chemical composition of the supported Pt-Ru catalyst was analyzed by Energy Dispersive X-ray Spectroscopy (EDS) coupled to the HREM. It was possible to obtain a qualitative analysis of the amount of Pt and Ru in the catalyst as well as any other chemical element that could appear as product of the synthesis procedure. Figure 4 shows the composition analysis spectrum of the Pt-Ru catalyst obtained by EDS. The atomic percentage of Pt in the sample was 14.09% and for the case of Ru the composition ratio was 85.91%. It was clearly observed that synthesizing Pt-Ru by carbonyl-metal complex reduction process it is possible to produce a Ru-enriched and nanostructured catalyst based on Pt-Ru. The low content of Pt in the catalyst can be attributed to the reactions pro-

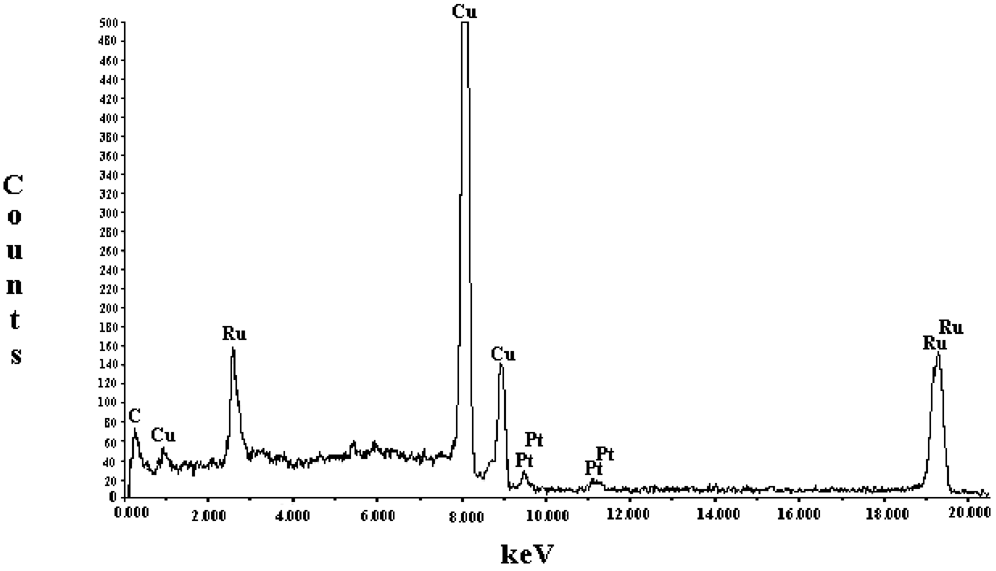

Figure 4. Composition analysis of the supported Pt-Ru catalyst obtained by EDS.

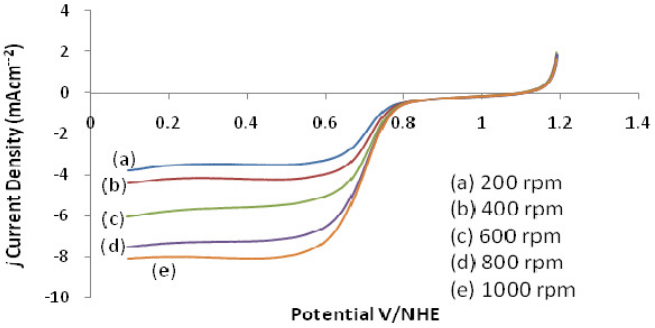

Figure 5. Polarization curves of Ru enriched Pt-Ru catalyst for the Oxygen Reduction Reaction in 0.5 M H_2SO_4 solution at different rotating rates.

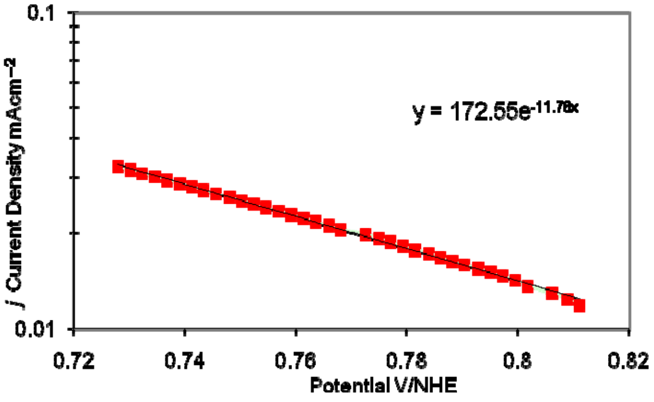

Figure 6. Corrected Tafel plots of the Ru enriched Pt-Ru/C catalyst.

moted by carbonyl decomposition of Pt where the temperature, concentration and decomposition rate of Ru carbonyl affected the formation of bimetallic nanoparticles. The experimental conditions for obtaining Ru enriched Pt-Ru nanostructured catalyst allowed the formation of the bimetallic material without the presence of Cl as the principal agent present in the Pt precursor (Figure 4). Cu signal in EDS spectrum was due to the composition of the substrate used for analyzing the sample.

3.1. Electrochemical Analysis of Ru enriched Pt-Ru nanostructured catalyst

The polarization curves for the oxygen reduction reaction (ORR) in acidic medium of the synthesized catalyst are shown in Figure 5. One can find a linear dependence in the increment of cathodic current density as a function of the rotating rate of the working electrode indicating the catalytic nature of the sample. The oxidation threshold of this system at low overpotentials was observed at 0.8 V/NHE and it corresponds to a catalytic system based on nanostructured platinum. There are three well defined regions in the ORR as shown in Figure 5: Region I where the system is controlled by the charge transfer mechanism and there is no variation of current as a function of the rotating rate, it occurred from 0.8 V to 0.75 V/NHE. This very short region in over-potential (about 0.5 V/NHE) is characteristic of the very active catalysts based on Pt, in this case, nanostructured Pt. Region II (from 0.75 V to 0.6 V/NHE) is characterized by the mixed control of the charge transfer and the mass transport mechanisms, and Region III from 0.6V to 0.1 V/NHE, characterized by plateau regions associated to the complete control of the system by mass transport. The limiting currents obtained at every rotating rate in this region produced the diffusion current density values for the system rotating from 200 rpm to 1000 rpm. The Ru enriched Pt-Ru catalyst showed the establishment of three regions forming the ORR response. It is possible to consider that the kinetic and diffusion mechanisms carried out by the cata-

Table 1. Kinetic parameters of the Ru enriched Pt-Ru System for the Oxygen Reduction Reaction in acidic medium.

	OCP (V/NHE)	-b (mV/Dec)	nα	n	J_o *10^{-5} (A·cm^{-1})	E (V/NHE)	h (V)
Pt-Ru/C	0.75	195	0.304	4	9.12	0.73-0.81	0.449

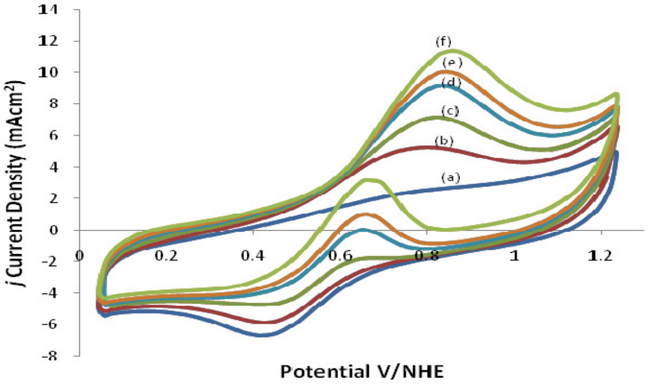

Figure 7. Cyclic voltammetries of Ru enriched Pt-Ru in 0.5M H_2SO_4 + 1M CH_3OH at 25 celsius in aqueous solution. (a) Reference cycle without presence of methanol, (b) Cycle 20, (c) Cycle 40, (d) Cycle 60, (e) Cycle 80, (f) Cycle 100.

lyst are well defined and the electron transfer and mass transport processes can be adequately analyzed by Koutecky-Levich approach. The analysis of $1/J=1/J_k+1/J_d$ mechanism showed that the electron transfer is predominant of first order assisting 4 electrons for completing the reduction reaction. It was found by comparing the slope of the ORR experimental results to the theoretical line for n=4e-. Due to the platinic nature of the Ru enriched Pt-Ru/C catalyst, it is clearly thought that this catalyst follows the direct route to reduce oxygen according to the reaction: $O_2+4H^++4e^-\rightarrow 2H_2O$. All the current densities were referred to the calculated electrochemical active surface area of the working electrode in 0.5M H_2SO_4.

In figure 6 it is shown the Tafel plot for the Ru enriched Pt-Ru catalyst at low overpotentials (0.81 V to 0.73 V/NHE). The kinetic parameters such as the Tafel Slope (b), charge transfer coefficient (a) and exchange current density (I_0) are expressed in Table 1, and they were calculated by establishing the proper corrections to the total current in the Tafel analysis. The Tafel slope of 195 mV per decade obtained for the Ru enriched Pt-Ru catalyst is a good value for the Pt-Ru system used principally for alcohol oxidation, according to the slopes reported in previous works [14-16]. The kinetic values obtained for this catalytic material show its high activity for reduction processes in fuel cell environment.

In figure 7 it is shown the methanol oxidation reaction conducted by the Ru enriched Pt-Ru/C nanostructured catalyst. The oxidizing solution was 1M CH_3OH + 0.5M H_2SO_4 in aqueous medium at 25 Celsius, using an open electrochemical cell. The catalyst was tested for 100 cycles at 10 mV/sec scan rate. It was observed an adequate methanol oxidation reaction because the forward oxidation peak was increasing when the cycling was increasing too. The enrichment of Ru in the sample is probably the cause to observe as a good response in the methanol oxidation through the cyclic voltammetries shown in Figure 7. In the cycle 100 the forward oxidation peak was observed at 0.86 V/NHE, with a current density of j_f = 11.5 mAcm^{-1}. The backward oxidation peak was observed at 0.68 V/NHE, with a current density of j_b = 3.2 mAcm^{-1}. The forward and backward oxidation peak potentials corresponds to the reported commercial Pt/C [17]. It means that the Ru enriched Pt-Ru nanostructured catalyst has the performance of a platinic material and the excess of Ru contributes to complete the oxidation reaction of intermediate species such as CO. It can be considered because the ratio j_b/j_f has a value of 0.28 (in commercial Pt/C the normal j_b/j_f value is 0.74), and it shows that the catalyst promotes the oxidation of methanol with a minimum self-poisoning of the catalyst by presence of adsorbed water or CO species [18,19]. Further studies are needed to evaluate the performance of Ru enriched Pt-Ru nanostructured catalyst obtained by carbonyl-metal complex reduction as an appropriate catalytic material in experimental Direct Methanol Fuel Cells.

4. CONCLUSION

Ru enriched Pt-Ru catalyst was synthesized by carbonyl-metal complex reduction. It was possible to observe the nanostructured nature of the material. The electrochemical characterization showed that Ru enrichment did not affect the platinic performance of the catalyst in the oxygen reduction reaction but it is an important element for improving the performance of the methanol oxidation reaction. It was possible to infer semi-quantitatively the influence of the excess of Ru in the good performance of the catalyst over 100 cycles of methanol electro-oxidation.

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