A Comparative Study of the Catalytic Performance of Pt-Based Bi and Trimetallic Nanocatalysts Towards Methanol, Ethanol, Ethylene Glycol, and Glycerol Electro-Oxidation

Hadla S. Ferreira¹, Martin Gocyla², Hadma S. Ferreira³, Rennan G. O. Araujo³, Caio V. S. Almeida¹,⁴, Marc Heggen², Rafal E. Dunin-Borkowski², Katlin I. B. Eguiluz¹,⁴, Peter Strasser⁵, and Giancarlo R. Salazar-Banda¹,⁴

¹Laboratório de Eletroquímica e Nanotecnologia, Instituto de Tecnologia e Pesquisa, CEP: 49032-490, Aracaju-SE, Brazil
²Ernst-Ruska Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
³Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Ondina, 40.290-170, Salvador, Brazil
⁴Programa de Pós-Graduação em Engenharia de Processos, Universidade Tiradentes, CEP: 49032-490, Aracaju-SE, Brazil
⁵Department of Chemistry, Technical University Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany

Carbon-supported platinum is used as an anode and cathode electrocatalyst in low-temperature fuel cells fueled with low-molecular-weight alcohols in fuel cells. The cost of Pt and its low activity towards the complete oxidation of these fuels are significant barriers to the widespread use of these types of fuel cells. Here, we report on the development of PtRhNi nanocatalysts supported on carbon made using a reduction chemistry method with different atomic rates. The catalytic activity of the developed catalysts towards the electro-oxidation of methanol, ethanol, ethylene glycol, and glycerol in acidic media was studied. The obtained catalysts performances were compared with both commercial Pt/C and binary Pt₇₅Ni₂₅/C catalyst. The nanostructures were characterized, employing inductively coupled plasma optical emission spectrometer, X-ray diffraction, scanning transmission electron microscopy, and energy-dispersive X-ray spectroscopy. The binary catalyst presents a mean particle size of around 2 nm. Whereas the ternary catalysts present particles of similar size and with some large alloy and core–shell structures. The alcohol oxidation onset potential and the current density measured after 3600 s of chronoamperometry were used to classify the catalytic activity of the catalysts towards the oxidation of methanol, ethanol, ethylene glycol, and glycerol. The best PtRhNi/C catalyst composition (i.e., Pt₄₃Rh₃₂Ni₁₄/C) presented the highest activity for alcohols oxidation compared with all catalysts studied, indicating the proper tuning composition influence in the catalytic activity. The enhanced activity of Pt₄₃Rh₃₂Ni₁₄/C can be attributed to the synergic effect of trimetallic compounds, Pt, Ni, and Rh.

Keywords: Nanostructured Materials, Core–Shell, Alcohols Electrooxidation, Fuel Cell.

1. INTRODUCTION

Since the first scientific publication on fuel cells in the nineteenth century to nowadays, significant progress has been achieved regarding the development of fuel cell technologies for different commercial applications [1–3]. In the automotive sector, for example, the primary focus has been the innovation of the membrane-electrode-assembly (MEA) systems for H₂-fuel cells and direct alcohol fuel cell (DAFCs), once these are easily degraded by contaminants such as CO and humidity from feed gases of the cell [4–6]. The DAFCs are considered excellent candidates for vehicle engines because they can
operate using liquid fuels, such as methanol and ethanol (renewable), besides it can operate at low temperature (80–90 °C), which is satisfactory from the environmental viewpoint [7–9]. Regardless of all the advantages exhibited by DAFCs, there are still some limitations that must be overcome before the development of a definitive commercial technology.

In contrast to direct methanol fuel cells (DMFCs), DEFCs (direct ethanol fuel cells) show additional advantages such as high energy density (6.09 kWh kg⁻¹ vs. 8.00 kWh kg⁻¹, respectively), increased cell efficiency, due to lower cross-over of fuel, and, lower environmental impact since ethanol is the main product drag out from sugar cane, a renewable source [10]. Furthermore, compared with the methanol, ethanol has a higher boiling point (78.3 to 64.5 °C), lower toxicity, and it is easier to store [11]. Moreover, in recent years, other alcohols (e.g., propanol, [12] ethylene glycol, [13] and glycerol [14]) have been proposed as alternative fuels in DAFCs.

Currently, the research in this area has been focused on the development of the electrocatalysts alternative to Pt-based materials in order to reduce the high cost associated to large amounts of platinum used as electrodes (both cathode and anode) and increase its resistance to CO poisoning; besides to enhance their catalytic activity and selectivity. It is well established that the incomplete oxidation of alcohols leads to the formation of CO and other intermediary by-products that may adsorb on Pt catalytic sites, thus decreasing the performance of the electrode. As a common consensus, the selectivity to CO₂ in the oxidation reaction depends on the mechanism of breaking C–C or C–H bonds over the catalytic sites. In this sense, the addition of second and third metal to Pt-based catalysts improved the catalytic activity towards alcohols electro-oxidation [13–17].

The addition of Ni to Pt catalyst can reduce the high cost of catalysts, due low cost of Ni, and improve the catalyst performance during the oxidation reaction due to the synergistic effect between nickel and platinum. Thus, enhanced activity towards methanol and ethanol oxidation reactions are attributed to the bifunctional mechanism and the electronic interaction between Ni and Pt [18, 19]. On the other hand, PtRh bimetallic catalysts also showed strong potential to oxidize alcohol molecules. Some authors observed that the presence of the rhodium, improved C–C bond breaking, and increases the selectivity towards the formation of CO₂, compared with pure platinum-based electrodes [20–23]. The addition of Rh as a third element to Pt-based catalysts has also been studied in electro-oxidation of alcohols [24], and these ternary catalysts are considered promising candidates for ethanol electro-oxidation [25].

Here, we synthesized and compared the performances of ternary and binary catalysts (PtRhNi/C and PtNi/C), prepared with three different molar ratios of metals, towards the oxidation of methanol, ethanol, ethylene glycol, and glycerol in acidic medium. The catalytic activities of the developed catalysts were compared with a commercial Pt/C catalyst. The catalysts were characterized by inductively coupled plasma optical emission spectrometry (ICP OES), X-ray diffractometry (XRD), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) coupled to the TEM equipment.

2. EXPERIMENTAL DETAILS

2.1. Chemicals and Materials

Commercially available reagents were used in the synthesis of all catalysts. Hexachloroplatinic acid (H₃PtCl₆⋅H₂O—37.50% Pt basis), nickel chloride (NiCl₂—≥99%), rhodium chloride (RhCl₃—98%), formic acid (HCOOH—≥98%), ethylene glycol (HOCH₂CH₂OH—99.8%), sodium borohydride (NaBH₄—99.99%), acid citric (HOC(COOH)(CH₂COOH))₃—≥99.5%) sulfurous acid (H₄SO₄—95.0–98.0%), methanol (CH₃OH—≥99.8%), ethanol (CH₃CH₂OH—≥99.8%), glycerol (HOCH₂CH(OH)CH₂OH—≥99.5%), were all purchased from Sigma-Aldrich. Vulcan XC-72R® (250 m²/g) was purchased from Cabot Corporation. All solutions were freshly prepared with ultrapure water (18 MΩ) purified by an MS 2000 system from Gehaka.

2.2. Catalyst Preparation

2.2.1. Synthesis of Unsupported Ni Nanoparticles

Nickel nanoparticles were synthesized using a polyol chemical reduction method [26]. A 0.05 mol L⁻¹ nickel chloride solution (metallic precursor) and ethylene glycol were added to a 125 mL round flask. In the sequence, the solution was heated to 140 °C. At this temperature, 1.0 g of NaBH₄ was added under magnetic stirring, and black color was observed immediately after NaBH₄ addition. The system was maintained under magnetic stirring at 140 °C for 3 h. Subsequently, the nanoparticles were separated by centrifugation, washed with ethanol and dried at room temperature.

2.2.2. Synthesis of PtNi/C

The PtNi/C catalyst was prepared by sequential impregnation of the platinum nanoparticles on the Ni nanoparticles; as previously described. The Ni nanoparticles were added to a proper amount of H₃PtCl₆·H₂O aqueous solution, maintaining an atomic ratio of 3:1 (Pt/Ni), and uniformly dispersed by ultrasound for 30 min. 20 % of formic acid was added to the mixture, and the system was stirred at 70 °C for 1 h. Then, the nanoparticles were dispersed on carbon black to produce 20% of metallic mass loading in the catalyst. After this, it was sonicated for another 30 min and stirred overnight at room temperature. The resulted slurry was filtered, washed several times with water and dried at 70 °C for 12 h.
2.2.3. Synthesis of PtRhNi/C

For preparation of the PtRhNi/C catalyst, Pt and Rh precursors were added to Ni nanoparticles, in the different atomic ratios 3:1 (Pt/Rh), 3:2 (Pt/Rh) or 3:3 (Pt/Rh), following a similar protocol as used for PtNi/C catalyst. The resultant Pt–Rh–Ni catalysts had nominal Pt:Rh:Ni atomic ratio of 3:x:1, with x values varying from 1 to 3.

2.3. Electrochemical Measurements

An Autolab Model PGSTAT 302N potentiostat/galvanostat was used for the electrochemical measurements. The experiments were performed at room temperature using a three-electrode electrochemical glass cell system. The electrodes used were a glassy carbon working electrode (as support for the catalytic composites, with 3 mm in diameter) a Pt foil counter electrode and a reversible hydrogen electrode (RHE) as the reference. In order to prepare the working electrode, 10.0 mg of each electrocatalyst powder was suspended in 3.5 mL of isopropanol and 50 µL of 5 wt% Nafion® solution under sonication for 30 min to form a uniform ink. Later, 5 µL of this ink was pipetted onto the glassy carbon support surface, dried in air and afterward hydrated in ultrapure water. Cyclic voltammetry and chronoamperometry experiments (at 0.6 V vs. RHE) were performed in 0.5 mol L⁻¹ H₂SO₄, as well as in 0.5 mol L⁻¹ methanol, ethanol, ethylene glycol or glycerol. The electrochemical cell was purged for 15 min with N₂ before each experiment.

2.4. Physical Characterization

An inductively coupled plasma optical emission spectrometer with an axial view (model 720, View Pro, Agilent Technologies, Penang, Malaysia) and a solid-state detector was used for the determination of the chemical composition of the catalysts. All solutions and samples were measured and analyzed. External calibration was used for the calibration curves were made in concentrations from 2.5 up to 30.0 mg L⁻¹ for Ni and Rh, using six concentrations including the blank.

The structural characterization of the catalysts was made by XRD in a Bruker D8 Advance diffractometer (Billerica, Massachusetts, USA) operated with a Cu source (Kα = 1.5418 Å) at a voltage of 30 kV, a current of 10 mA and a Lynx Eye Detector. Measurements were carried out in 2θ = 10–90° with a step of 0.03° for 0.4 s. Bragg peak positions were compared with the reference XRD patterns (PDF data files, National Institute of Science and Technology).

STEM measurements were performed using an FEI Titan 80-200 (“ChemiSTEM”) electron microscope with a Cs-probe corrector (CEOS GmbH) and a HAADF detector. The microscope was operated at 200 kV. In order to achieve “Z-Contrast” conditions, a probe semi-angle of 25 mrad and an inner collection semi-angle of the detector of 88 mrad were used. Compositional maps were obtained by EDX using four large-solid-angle symmetrical Si drift detectors. For EDX elemental mapping, Pt L, Rh L, and Ni K peaks were used. The error of the EDX composition measurement is ±1–2 at%.

3. RESULTS AND DISCUSSION

3.1. Physical Characterization

The metallic composition of the catalysts (respective molar ratios) analyzed by ICP-OES (Table I) is similar to the nominal compositions demonstrating the feasibility of the method to produce nanostructures with the desired composition.

The HAADF-STEM image of the bimetallic PtNi/C catalyst, in Figure 1, demonstrates the presence of very small nanoparticles with an average size around 2 nm. Overall, particle agglomeration was not observed. Therefore, the synthesis method used, without the presence of surfactants, was efficient to obtain well-dispersed catalyst nanoparticles with an average size below 3 nm. These characteristics are considered ideal for improved catalytic activities.

The HAADF-STEM images of the ternary Pt–Rh–Ni/C catalysts in Figure 2 show tiny and well-dispersed nanoparticles on the carbon support showing, however, some bigger nanoparticle agglomerates.

A combined high-resolution HAADF-STEM and corresponding EDX investigation (Fig. 3) revealed the formation of a Pt–Ni alloy for Pt₅₃Rh₂₈Ni₁₈/C (Fig. 3(a)) and the presence of core–shell-like nanostructures with Rh mainly in the shell for the Pt₆₀Rh₂₀Ni₂₀/C (Fig. 3(c)). Possibly, rhodium covered a small portion of the Pt added in the Pt₄₅Rh₂₈Ni₈/C catalyst, forming a core–shell structure (Pt(core)@Rh(shell)). Conversely, the Pt₆₀Rh₂₀Ni₂₀/C catalyst did not form core–shell structures (Fig. 3(b)). The EDX maps of the Pt₄₅Rh₂₈Ni₁₈/C catalyst sample (Fig. 3(c))

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Nominal ratio (Pt:Rh:Ni)</th>
<th>Atomic ratio (Pt:Rh:Ni)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt₅₃Rh₂₈Ni₁₈/C</td>
<td>75:25</td>
<td>77:23</td>
<td>0.3903</td>
</tr>
<tr>
<td>Pt₆₀Rh₂₀Ni₂₀/C</td>
<td>60:20:20</td>
<td>61:20:19</td>
<td>0.3879</td>
</tr>
<tr>
<td>Pt₅₄Rh₂₈Ni₁₈/C</td>
<td>54:28:18</td>
<td>55:27:18</td>
<td>0.3867</td>
</tr>
<tr>
<td>Pt₅₃Rh₂₁Ni₁₉/C</td>
<td>43:43:14</td>
<td>44:42:14</td>
<td>0.3862</td>
</tr>
</tbody>
</table>

Note: *ICP-OES.
show the formation of a ternary core–shell-like structure with Ni and Pt in the core and local enrichment of Rh in the outermost part of the nanoparticle (see arrows in Fig. 3(c)). The Pt$_{75}$Rh$_{25}$/CNi$_{14}$ catalyst (Figs. 3(d and e)) shows a combination of core–shell-like nanostructures decorated very small (~2 nm) alloy nanoparticles, as will be discussed hereafter from XRD data.

Figure 4 shows the XRD powder patterns for each developed catalyst. The diffraction peak at approximately 25° corresponds to the plane (002) for the hexagonal structure of carbon support used in the catalysts. The Pt$_{75}$Ni$_{25}$/C, Pt$_{60}$Rh$_{20}$Ni$_{20}$/C, Pt$_{54}$Rh$_{28}$Ni$_{18}$/C and Pt$_{43}$Rh$_{43}$Ni$_{14}$/C catalysts profiles reveal five main symmetrical diffraction peaks, which correspond to the (111), (200), (220), (311) and (222) facets of the face-centered cubic (fcc) structure of Pt. The Pt (111) and Rh (111) diffraction peaks were observed at 40.16°, 40.39°, 40.57°, and 40.63°, respectively for Pt$_{75}$Ni$_{25}$/C, Pt$_{60}$Rh$_{20}$Ni$_{20}$/C, Pt$_{54}$Rh$_{28}$Ni$_{18}$/C and Pt$_{43}$Rh$_{43}$Ni$_{14}$/C catalysts, which shift from the values of 2θ corresponding to pure Pt (111) and Rh (111) values of 39.764 and 41.069°, respectively (PDF, ICSD 041525). Pt and Rh diffraction peaks could not be resolved separately due to the proximity of the 2θ values for these two elements.

The diffraction peaks shift further to higher angles, indicating the incorporation of Rh and Ni into the Pt metal structure. More intense displacements happen with the increase of Rh content in the catalysts. These results indicate the formation of PtNi alloy in the binary and PtRhNi alloy to ternary catalysts [27]. Due to the formation of alloy, a lattice contraction occurs because of the substitution of smaller nickel and rhodium atoms for larger platinum atoms. This effect contributes to the downward shift of the d-band center and therefore could weaken the CO adsorption onto the Pt surface, and consequently, higher tolerance of CO is expected. Thus, the lattice parameter for all catalysts (displayed in Table I) was lower than that of the Pt (a = 0.3970 nm, ICSD 041525).

Figure 5(a) shows the cyclic voltammograms obtained for catalysts in 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution. All catalysts show peaks of chemisorbed hydrogen, ranging from 0.05 to 0.35 V. The hydrogen adsorption/desorption peaks for the binary Pt$_{75}$Ni$_{25}$/C catalyst are more defined than that of the commercial Pt/C, due to changes in the Pt crystal lattice by the addition of Ni atoms.

The ternary PtRhNi/C catalysts showed changes in the hydrogen desorption/adsorption region when compared with Pt$_{75}$Ni$_{25}$/C and commercial Pt/C. A unique peak at 100 mV is observed for these catalysts, which may be associated with hydrogen adsorption/desorption in an intermetallic Pt–Rh phase.

Electrochemical surface areas (ECSA) of the catalysts were calculated by integration of the CO stripping curves. A total charge of 420 µC cm$^{-2}$ was assumed for the oxidation of a monolayer of linearly adsorbed CO [28]. The ECSA of the catalysts Pt$_{60}$Rh$_{20}$Ni$_{20}$/C, Pt$_{54}$Rh$_{28}$Ni$_{18}$/C, Pt$_{43}$Rh$_{43}$Ni$_{14}$/C, Pt$_{75}$Ni$_{25}$/C are 0.923 cm$^2$, 0.956 cm$^2$, 0.803 cm$^2$ and 0.714 cm$^2$ respectively. The higher ECSA values found for the ternary catalysts indicate they have more accessible active sites toward alcohols oxidation. Comparing the CO stripping behaviors (Fig. 5(b)), all catalysts present a lower potential for CO electrooxidation than the commercial Pt/C, suggesting an enhanced CO-tolerance on Pt-based bi- and trimetallic nanocatalysts with Ni and Rh, in agreement with literature data. The CO stripping peaks on Pt$_{75}$Ni$_{25}$/C, Pt$_{60}$Rh$_{20}$Ni$_{20}$/C, Pt$_{54}$Rh$_{28}$Ni$_{18}$/C and Pt$_{43}$Rh$_{43}$Ni$_{14}$/C were located at 0.71, 0.68, 0.66, and 0.65, respectively. The CO stripping peak on Pt$_{43}$Rh$_{43}$Ni$_{14}$/C was shifted in 180 mV to more negative potentials compared with that on Pt/C (0.83 V).
3.2. Catalytic Activity Toward Electrooxidation of Alcohols

The electrocatalytic performance of the ternary catalysts was evaluated as a function of the alcohol investigated: methanol, ethanol, ethylene glycol and glycerol at room temperature and the results were compared with the Pt75Ni25/C binary and commercial Pt/C (Alfa Aesar). The current densities were normalized by the specific activity from CO stripping.

3.2.1. Catalytic Activity Towards Methanol Oxidation

Figure 6 shows the cyclic voltammetry profiles and chronoamperometric measurements for the oxidation of methanol. The voltammetric profiles (Fig. 6(a)) consist of two well-defined peaks at the forward and backward scans. The peak at the forward scan originates from the oxidation of methanol molecules, while the one at the backward is assigned to oxidation of methanol and their reaction intermediates on the clean surface of the catalysts after oxides reduction.

The maximum current density of the Pt43Rh43Ni14/C, Pt54Rh28Ni18/C, Pt60Rh20Ni20/C were 0.34, 0.29 and 0.41 mA cm$^{-2}$, respectively, while the current peak of Pt75Ni25/C and Pt/C Alfa Aesar are 0.42 and 0.11 mA cm$^{-2}$, respectively. When comparing Pt/C and Pt75Ni25/C performances, note that the Pt75Ni25/C catalyst overcomes the Pt/C current densities from over 0.60 V (Inset in Fig. 6(a)). This behavior can be a result of the electronic effects of nickel atoms on Pt atoms that contribute actively to methanol oxidation.

The onset potential for the ternary PtRhNi/C catalysts is lower than for Pt75Ni25/C and Pt/C Alfa Aesar. It suggests facile oxidation of methanol on PtRhNi/C catalysts, due to the presence of the rhodium that can produce enough oxygen species at a low potential, decreasing the energy needed for the reaction [29]. Notably, the shift of the oxidation onset potential towards lower potentials is higher with the increasing of Rh content in the catalyst. The Pt43Rh43Ni14/C catalyst exhibited a shift in the peak potential of 90 mV related to Pt/C Alfa Aesar. Notably,
the presence of Rh and Ni improves the activity towards methanol oxidation due to the chemical states of Rh and Ni [30].

The ratio of the forward peak current density and the backward current density \( (I_f/I_b) \) has been used to estimate the poisoning tolerance of the catalysts to carbonaceous species (such as CO) formed during methanol oxidation [31, 32]. The \( I_f/I_b \) values obtained for Pt75Ni25/C, Pt60Rh20Ni20/C, Pt54Rh28Ni18/C, and Pt43Rh43Ni14/C catalysts were 1.2, 1.8, 1.9 and 2.7, respectively, which are higher than of the Pt/C Alfa Aesar (1.0), suggesting less accumulated residues on the catalyst during methanol oxidation and thus enhanced catalytic activity. Among all the catalysts investigated, Pt43Rh43Ni14/C had the highest \( I_f/I_b \) rate, which further evidence that an increased amount of rhodium on the carbon surface could effectively improve the tolerance of Pt catalysts to CO poisoning.

Chronoamperometric measurements (Fig. 6(b)) confirmed a better tolerance of the Pt43Rh43Ni14/C catalyst to the intermediate carbonaceous species produced during the oxidation of methanol at 0.6 V. The current density of methanol oxidation for Pt43Rh43Ni14/C is the highest among all the investigated catalysts. After 3600 s of the experiment, the current density was about 0.015 mA cm\(^{-2}\) for Pt43Rh43Ni14/C that is 5.0-fold larger than that on the Pt/C Alfa Aesar catalyst (0.003 mA cm\(^{-2}\)). Presumably, the Pt43Rh43Ni14/C catalyst produces more oxygen species at low potentials, which has a higher amount of rhodium on the surface. Pt75Ni25/C, Pt60Rh20Ni20/C, and Pt54Rh28Ni18/C catalysts exhibit higher current densities than commercial Pt/C, indicating a relatively stable electrochemical activity and a better tolerance to the intermediate carbonaceous species during the oxidation of methanol.

3.2.2. Catalytic Activity Towards Ethanol Oxidation

Figure 7 shows cyclic voltammograms and chronoamperometric measurements for all catalysts in the presence of ethanol. In the cyclic voltammograms for the oxidation of ethanol (Fig. 7(a)), for all catalysts, the hydrogen adsorption/desorption region is suppressed by adsorbates from
alcohol decomposition formed on Pt surface [33]. Moreover, the addition of nickel to Pt increases the current densities and decreases the onset potential. These outcomes could result from a bifunctional mechanism as well as to electronic effect between Pt and Ni that favor the ethanol oxidation, as related in other reports for binary Pt-based catalysts [18]. Besides, the current density is higher for the Pt60Rh20Ni20/C catalyst than for all other catalysts.

Nevertheless, the current density values estimated at 0.8 V indicate superior specific activities in the following decreasing order: Pt60Rh20Ni20/C > Pt43Rh43Ni14/C > Pt54Rh28Ni18/C > Pt75Ni25/C > commercial Pt/C. Besides, these catalysts show current densities 5.0, 4.3, 4.0, and 2.8 times higher than Pt/C Alfa Aesar, respectively. The higher the current density, the higher the ethanol amount being oxidized.

The enhanced current densities values at the ternary catalysts indicate that the introduction of Rh into the binary catalysts augments the electrocatalytic activity towards ethanol oxidation. Possibly, the Rh offers active sites for the adsorption of alcohol molecules and promotes the breaking of C–C bonds of these molecules. The synergistic effect between Pt and Rh facilitate the oxidation of ethanol at low potentials, as already demonstrated by Gupta and Datta [33]. These authors studied the activity of PtRh alloy electrodes with different compositions towards the electrooxidation of ethanol and observed that the enhanced electrocatalytic activity of PtRh catalyst results from an improvement of C–C bond dissociation rather than to a bifunctional mechanism.

The onset potentials for the oxidation of ethanol (measured at 0.02 mA cm$^{-2}$) were 0.40 V, 0.44 V, 0.46 V, 0.48 V and 0.68 V for Pt60Rh20Ni20/C, Pt54Rh28Ni18/C, Pt43Rh43Ni14/C, Pt75Ni25/C, and Pt/C Alfa Aesar catalyst, respectively. As stated before, the synergetic interaction between Rh, Ni, and Pt in the Pt43Rh43Ni14/C, Pt54Rh28Ni18/C, and Pt60Rh20Ni20/C catalysts result in lower onset potentials.

However, among the ternary catalysts, the Pt60Rh20Ni20/C catalyst exhibits the highest peak current density. This outcome may be due to the presence of Rh in the smallest quantity in this catalyst. For Pt43Rh43Ni14/C and Pt54Rh28Ni18/C catalysts, some Rh nanoparticles may have blocked the active sites of Pt, due to the formation of Pt@Rh core–shell structures (See Fig. 3). Hereafter, due to the complexity of the reaction mechanism of alcohols with C–C bonds, we do not use the $I_p/I_b$ ratio as a parameter to evaluate the performance of the developed catalysts towards ethanol, glycerol, and ethylene glycol oxidation.

Chronoamperometric measurements (Fig. 7(b)) also indicate the best activity and reaction stability of the Pt43Rh43Ni14/C catalyst for the oxidation of ethanol. After 3600 s of chronoamperometry, the current density for Pt43Rh43Ni14/C was 3.1-fold higher than for commercial Pt/C. Besides, the Pt60Rh20Ni20/C and Pt54Rh28Ni18/C catalysts show lower reaction stability.
catalysts exhibit higher current density values over the entire range of experimental time compared with Pt53Ni25/C and Pt/C Alfa Aesar catalysts. The decrease in the current density is due to the presence of intermediate species. Rh and Ni in higher amounts could favor the formation of oxygenated species in excess which can block the active sites of Pt and difficult the oxidation of the adsorbed intermediate species and increase the selectivity towards CO2 [33, 34].

3.2.3. Catalytic Activity Towards Ethylene Glycol Oxidation

The oxidation reaction of ethylene glycol was investigated to clarify the role of Ni and Rh on the catalytic performance in the presence of a C–C bond. The cyclic voltammograms of the binary and ternary catalysts, in Figure 6, display two peaks in the forward scan. For ternary catalysts, the first peak is about 0.75 V and the second is around 0.86 V. While the Pt53Ni25/C catalyst displays the first peak at about 0.79 V. It is a result of the partial oxidation of ethylene glycol to C2 by-products [35]. On the other hand, Pt/C Alfa Aesar catalyst exhibited only one peak at 0.85 V and both with Pt53Ni25/C catalyst, two quasi-overlapped peaks in the reverse scan, which can be a result of the dissociation of ethylene glycol to CO.

In Figure 8(a) the current densities for ethylene glycol oxidation increase similarly of current densities for ethanol oxidation (Fig. 7(a)). However, these values are lower than for the ethanol oxidation, suggesting a poisoning of the catalysts by reaction intermediates produced during the oxidation of ethylene glycol (e.g., glycolic and oxalic acids) and an ethylene glycol dissociation to COads. The maximum current density values at 0.8 V for Pt60Rh20Ni20/C, Pt41Rh43Ni16/C, Pt54Rh24Ni18/C, Pt58Ni25/C

A Comparative Study of the Catalytic Performance of Pt-Based Bi and Trimetallic Nanocatalysts

**Ferreira et al.**

The same behavior was observed during the oxidation of ethanol (Fig. 7(b)). The higher stability and poisoning tolerance for Pt$_{43}$Rh$_{43}$Ni$_{14}$/C could be a consequence of the higher amounts of Rh that favor the formation of oxygenated species. All the binary and ternary catalysts exhibited higher current density compared with Pt/C Alfa Aesar.

### 3.2.4. Catalytic Activity Towards Glycerol Oxidation

Finally, the effect of the combined use of Ni, Rh, and Pt was evaluated on the oxidation of glycerol. Similarly, to the observed for the oxidation of ethylene glycol (Fig. 8(a)), the binary and ternary catalysts show two peaks in the first forward scan (Fig. 9(a)). One maximum peak at around 0.73 V and a second peak at 0.84 V. The Pt/C Alfa Aesar catalyst shows different shape of the cyclic voltammetry profile compared with binary and ternary catalysts.

Figure 8. (a) Cyclic voltammograms curves (second cycle) of Pt/C Alfa Aesar, Pt$_{54}$Rh$_{28}$Ni$_{18}$/C, Pt$_{60}$Rh$_{20}$Ni$_{20}$/C, Pt$_{75}$Ni$_{25}$/C, and Pt/C Alfa Aesar catalysts and a scan rate of 20 mV s$^{-1}$. (b) Chronoamperograms after application of 0.6 V. Experiments taken in a 0.5 mol L$^{-1}$ H$_2$SO$_4$ and 0.5 mol L$^{-1}$ ethylene glycol solution at room temperature. Inset: Enlargement of the region between 0.3 and 0.7 V.

and Pt/C Alfa Aesar catalysts are 0.31, 0.26, 0.25, 0.20, and 0.09 mA cm$^{-2}$, respectively.

The onset potentials for the oxidation of ethylene glycol measured at 0.04 mA cm$^{-2}$ are 0.58, 0.59, 0.59, 0.60 and 0.70 V for Pt$_{43}$Rh$_{43}$Ni$_{14}$/C, Pt$_{60}$Rh$_{20}$Ni$_{20}$/C, Pt$_{54}$Rh$_{28}$Ni$_{18}$/C, Pt$_{75}$Ni$_{25}$/C, and Pt/C Alfa Aesar catalyst, respectively. Rh and Ni in the catalysts improve the formation of adsorbed OH species, freeing more active sites on the surface of the catalyst, thus making the oxidation of the intermediates more efficiently.

Figure 8(b) displays the stability, and the poisoning level of catalysts surfaces by the adsorption of intermediate species produced during the ethylene glycol oxidation. The current density of ethylene glycol oxidation on Pt$_{43}$Rh$_{43}$Ni$_{14}$/C was higher than all the catalysts investigated. After 3600 s, Pt$_{43}$Rh$_{43}$Ni$_{14}$/C presented current density 2.2-fold higher than Pt/C Alfa Aesar catalyst.

Figure 9. (a) Cyclic voltammograms curves (second cycle) of Pt/C Alfa Aesar, Pt$_{54}$Rh$_{28}$Ni$_{18}$/C, Pt$_{60}$Rh$_{20}$Ni$_{20}$/C, Pt$_{75}$Ni$_{25}$/C, and Pt/C Alfa Aesar catalysts and a scan rate of 20 mV s$^{-1}$. (b) Chronoamperograms after application of 0.6 V. Experiments taken in a 0.5 mol L$^{-1}$ H$_2$SO$_4$ and 0.5 mol L$^{-1}$ glycerol solution at room temperature. Inset: Enlargement of the region between 0.3 and 0.7 V.

exhibiting only a peak at 0.85 V. This can be rationalized as the outcome of a reaction, taking place on non-organized surfaces [36].

Considering the catalysts peak maximum height, a shift of 120 mV to more negative potentials related to commercial Pt/C occurred. Binary and ternary catalysts facilitate the oxidation of the glycerol. Zanata et al. [36] studying the electro-oxidation of glycerol on Rh-decorated PtIrO2 nanoparticles, observed that the presence of Rh facilitates the electro-oxidation of glycerol. Besides, the current density is higher for the catalysts synthesized than for the commercial Pt/C for all the potential range used for glycerol oxidation.

The bifunctional mechanism promoted by the rhodium and nickel presence decreases the onset oxidation potential and increases the current density.

The onset potentials for the glycerol oxidation measured at 0.02 mA cm−2 at the Pt43Rh43Ni14/C catalyst is 180 mV lower than for commercial Pt/C. Rh and Ni in the catalysts improve the formation of adsorbed OH species, freeing more active sites on the surface of the catalyst, thus making the oxidation of the intermediates more efficiently.

The maximum current density for glycerol oxidation was similar to the other alcohols: Pt60Rh20Ni20/C > Pt43Rh43Ni14/C > Pt40Rh20Ni20/C > Pt35Rh40Ni10/C > Pt75Ni25/C > Pt/C Alfa Aesar. However, the current density was lower than for the other alcohols studied due to sluggish kinetics for electro-oxidation of alcohols with three-carbon atoms.

Chronoamperometric experiments show the best stability for Pt43Rh43Ni14/C catalyst contrary to the lower stability exhibited for Pt/C (Fig. 9(b)). The higher amount of the oxophilic Rh can produce high amounts of oxygen species that promote the oxidation of adsorbed CO in the metallic sites [36], as well as improve the C–C bond cleavage [34]. In this sense, Huang et al. [37] investigated the glycerol oxidation mechanism at a molecular level on PtRh catalysts and observed that alloying Rh with Pt could enhance oxygen insertion reaction in the oxidation of glycerol.

In summary, the onset potentials observed for all the alcohols studied and the final chronoamperometric current density after 3600 s of tests indicate that the catalytic activity and oxidation stability decreases in the following order: Pt43Rh43Ni14/C > Pt40Rh20Ni20/C > Pt35Rh40Ni10/C > Pt75Ni25/C > Pt/C Alfa Aesar (as shown in Fig. 10 for chronoamperometric tests). The best activity of Pt43Rh43Ni14/C can be attributed to the synergic effect of trimetallic compounds and diverse catalysts structures (alloy and core–shell) as well as to the small particles size observed at this catalyst. Overall, the Pt43Rh43Ni14/C catalyst was more active to oxidize methanol and ethanol because in the oxidation of glycerol and ethylene glycol, other reaction intermediates (glycolic acid, and oxalic acid) and diverse products may be adsorbed during electro-oxidation process, besides COads causes poisoning of catalysts, and consequently decreasing the catalytic activity.

4. CONCLUSIONS

We have synthesized Pt-based binary, and ternary nanocatalysts supported on carbon with different atomic ratios (Pt:Rh:Ni) and investigated the electro-oxidation of different alcohols, which are being considered as alternative fuels in fuel cells. Using HAADF-STEM and EDX mapping the formation of various core–shell structures were verified presenting a rhodium shell and platinum core (Pt@Rh) structure and nickel and platinum core with rhodium in the shell (PtNi@Rh) in ternary catalysts, respectively. All catalysts were more active than the commercial Pt/C Alfa Aesar due to the electronic effect promoted by Ni and Rh in the structure of the platinum, which facilitates the oxidation of alcohols. The addition of Rh to the catalysts promoted a higher electrochemical performance towards the oxidation of the studied alcohols. Rh offers active sites for the adsorption of alcohol molecules, promoting the breaking of C–C bonds of these molecules. The Pt43Rh43Ni14/C was the most active in the electro-oxidation of alcohols at low potentials (around 0.6 V). These results could contribute to develop efficient catalytic materials for fuel cell anodes and help in the study of the electro-oxidation mechanism of alcohols.

Acknowledgments: The authors thank the Brazilian National Council of Technological and Scientific Development (CNPq, Brazil, grants: 303630/2012-4, 474261/2013-1, 407274/2013-8, 402243/2012-9, 400443/2013-9 and 310366/2018-6, 310282/2013-6), to the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil, grant: 001) and Fundação de Apoio à Pesquisa e à Inovação Tecnológica do Estado de Sergipe.

Figure 10. Summary of the catalytic activity of the developed catalysts towards methanol, ethanol, ethylene glycol and glycerol oxidation determined as the current density values taken from the chronoamperometric curves at 0.6 V after 3600 s.

References and Notes


Received: 30 April 2019. Accepted: 3 October 2019.