Oxygen reduction and hydrogen oxidation reactions on Ru-Fe electrocatalyst synthesized by a microwave-assisted synthesis

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Abstract
In this work, the oxygen reduction reaction in the absence or presence of 2.0 mol l\(^{-1}\) methanol and the hydrogen oxidation reaction are studied on RuFe electrocatalyst synthesized by a microwave thermal heating method in water as reaction medium. The electrocatalysts were morphologically and structurally typified by scanning electron microscopy and by x-ray diffraction, respectively. Three crystalline phases were found: Ru, Fe\(_2\)O\(_3\) and FeO\(_x\) (Bernalite). Functional tests were performed by convective (rotating disk electrode) and non-convective (linear sweep voltammetry and cyclic voltammetry) electrochemical techniques in 0.5 mol l\(^{-1}\) H\(_2\)SO\(_4\). Both RuFe electrocatalysts show interesting electrochemical activities since they can carry out both the oxygen reduction reaction and the hydrogen oxidation reaction.

1. Introduction
A proton-exchange membrane fuel cell (PEMFC) transforms, in one step and continuously, the chemical energy of a fuel (usually H\(_2\)) into electrical energy in one step, while the fuel and the oxidizing agent are supplied. When a PEMFC uses methanol (CH\(_3\)OH) as fuel, it is specifically called direct methanol fuel cell (DMFC) \([1]\). In comparison with traditional power generators, fuel cells show higher efficiency, they generate less noise and produce lower emissions of pollutants, among other properties. There are many kinds of fuel cells, but the PEMFC’s are one of the most important because of their applications in space programs, cars and industry \([2]\). The PEMFC’s have significant advantages that surpass other fuel cell types: null electrolyte leakage, shorter warm-up times and higher specific power \([3]\).

The two most significant and studied reactions in fuel cells are the ORR (oxygen reduction reaction) and the HOR (hydrogen oxidation reaction) because of their importance in energy technologies and industrial processes. The investigation in fuel cells aims to improve the efficiency and the kinetics of reactions and diminish the cost of the electrocatalysts used. The electrochemical reduction of molecular oxygen is the bottom line of many renewable energy technologies, e.g., PEM fuel cells \([2]\). Both PEMFC’s and DMFC’s typically use O\(_2\) as an oxidizing agent, which is reduced directly to water, through a direct mechanism (four-electron path, equation (1)). However, the ORR can also occur in several steps that involve side-products (peroxides), where the reduction is indirect (two-electron path, equations (2) and (3)).

\[
\begin{align*}
\text{O}_2 + 4e^- + 4H^+ & \rightleftharpoons 2H_2O \quad E^\circ = 1.229 \text{ V versus NHE} \\
\text{O}_2 + 2e^- + 2H^+ & \rightleftharpoons H_2O_2 \quad E^\circ = 0.695 \text{ V versus NHE}
\end{align*}
\]
The oxygen reduction is promoted on the surface of an electrode polarized by an electric potential. When it varies from the open circuit potential (OCP) in a cathodic direction a negative current is observed due to the oxygen reduction reaction. Conversely, when the electric potential changes in a positive fashion, electrons move from the electrolyte to the electrode and water is oxidized to produce oxygen, and a positive current is observed [1].

On the other hand, although the HOR activity of Pt is $10^7 - 10^9$ times higher than ORR, new materials with tolerance to carbon monoxide are being studied, which also aim to reduce the costs associated with the electrocatalyst [4]. Two HOR mechanisms in acidic media are reported [5]: the Tafel-Volmer mechanism, where there is a chemical adsorption of molecular hydrogen $MH_{ad}$ on the metallic surface (M), equation (4), and the Heyrovsky-Volmer mechanism, where there is an electrochemical adsorption of molecular hydrogen (equation (5)). Both processes are followed by a discharge path of the adsorbed hydrogen atom (equation (6)):

$$\text{H}_2 + 2\text{M} \rightleftharpoons 2\text{MH}_{ad}$$  \hspace{1cm} (4)

$$\text{H}_2 + \text{M} \rightleftharpoons \text{MH}_{ad} + \text{H}^+ + \text{e}^-$$  \hspace{1cm} (5)

$$\text{MH}_{ad} \rightleftharpoons \text{M} + \text{H}^+ + \text{e}^-$$  \hspace{1cm} (6)

Platinum and platinum alloys are the most popular electrocatalysts used in fuel cells; however, even though these materials have adequate performance, they have certain disadvantages such as ORR slow kinetics, relatively easy contamination of HOR by CO, high prices and long syntheses times. Hence, there is a keen interest in the electrocatalysis community to use alternative materials and more efficient methods of syntheses.

Several electrocatalysts used in fuel cells are synthesized using conventional methods such as pyrolysis, refluxing, solid-state syntheses, among others [6–11]. In general, these methodologies involve the use of organic solvents, long lasting of preparation and low efficiencies. In some of the conventional heating methods, the external heating source transfers the energy to the material via conduction and radiation, so the container temperature is higher than the reaction mixture, therefore this is a slow and inefficient method for transferring energy. Recently, the use of microwave radiation to produce new materials for PEMFC and DMFC has increased because of its advantages over conventional methods of synthesis. Some of these benefits are better efficiency, shorter synthesis times, uniform heating, and a potential for the development of materials with new properties (nanoparticles); another important feature is that water can be used as a reaction medium [12, 13]. Different materials synthesized by microwave irradiation have been reported in the literature: for example, Tsuji and collaborators [14] produced nanoparticles of Ag, Au, Pt, and AuPd in different organic solvents, while Hu and collaborators [15] reported the synthesis of a ZnO-graphene composite by photocatalytic reduction of Cr (VI). Liao and coworkers produced superparamagnetic materials as iron oxides (Fe$_2$O$_3$) [16]. In the Fuel Cells community, commercial electrocatalysts like Pt and PtRu have been synthesized using a microwave oven. Zhaolin Liu and collaborators [17] demonstrated improved activity in the presence of methanol, where these materials can be used as cathodes in a DMFC. On the other hand, Bernal López et al have reported the synthesis of metallic Ru electrocatalyst with activity for both the ORR and HOR using water as microwave absorbing media [18]. These are some examples of the versatility of microwave methodology applied in inorganic chemistry.

In this work, the microwave-assisted synthesis and characterization of RuFe electrocatalysts for the ORR and the HOR are presented. The electrocatalysts are synthesized using water as the reaction medium, thus avoiding the use of organic solvents. Water (a microwave-absorbing solvent) reached high temperatures and pressures during microwave heating and it begins to act more like an organic solvent, and thus some compounds become more soluble [12].

2. Experimental method

2.1. Synthesis of RuFe electrocatalyst

The electrocatalysts were synthesized at two different Ru:Fe molar ratios, 1:1 and 1:2, identified in this work as RuFe-1 and RuFe-2, respectively. Triruthenium dodecacarbonyl (Ru$_3$(CO)$_{12}$, 99% Aldrich) and iron trichloride hexahydrate (FeCl$_3$·6H$_2$O, 97% Aldrich) were used as precursors. They were ground and then mixed with 10 ml of deionized water (conductivity = 18.2 $\Omega$ cm$^{-1}$) in a PTFE-TFM tube. Then, they were inserted into an Anton Paar Synthos 3000 Microwave reactor and heated to 180 °C for 30 min by radiation (600 watts), with 30 min of cooling. The electrocatalysts thus obtained were separated and washed with deionized water thrice and dried at room temperature.
2.2. Structural and morphological characterization

Structural characterization was carried out by x-ray diffraction in a Bruker D8 Advance diffractometer (Cu Kα₁ radiation). The patterns were collected in a 2θ interval ranging from 10° up to 120°. The measured patterns were refined by the Rietveld method [19] using the GSAS code via the EXPGUI graphical interface [20, 21]. For surface morphology characterization, a JEOL JSM-7800F SEM was used to obtain scanning electron micrographs at 20 000× and 100 000× magnification. The parameters used in the microscope were: 3 kV, probe current of 3 nA, Upper Electron Detector (UED), Work Distances (WD) of 4.2 and 4.7 mm and Gentle Beam mode.

2.3. Electrochemical characterization

2.3.1. Electrode ink preparation and equipment

The electrochemical ink for the ORR studies was prepared by mixing 1.4 mg of Vulcan® XC-72 (Cabot) and 0.6 mg of the catalyst with 5 μl of Nafion® solution (Electrochem, 5%) and 15 μl of isopropyl alcohol (J T Baker, 99.90%). For the HOR, the electrochemical ink was prepared by mixing 0.7 mg of Vulcan® XC-72 with 0.3 mg of the catalyst, 250 μl of Nafion® solution and 250 μl of isopropyl alcohol. Both mixtures were sonicated for 5 min on a Cole-Palmer sonicator; 2 μl of the resulting slurry were deposited on the glassy carbon disk electrode (whose geometrical surface area is 0.1963 cm²) and dried at room temperature.

Electrochemical measurements were performed in a cell with a three-electrode configuration (reference: Hg/HgSO₄/0.5 mol l⁻¹ in sulfuric acid; counter: graphite rod), using 0.5 mol l⁻¹ H₂SO₄ (pH = 0.30) as conductive electrolyte. A glassy carbon disk electrode operated with the speed control unit (AMETEK, 616A) was utilized for the RDE studies. Electrochemical data were acquired by a bipotentiostat (Wave Driver) controlled by the AfterMath® software.

2.3.2. Cyclic voltammetry

Prior to the ORR and HOR studies, the electrocatalyst electrode surface was activated with cyclic voltammetry sweeps, scanned (in the electrolyte saturated with UHP N₂; Infra) between 0 and 0.98 V/NHE at 20 mV s⁻¹ (30 cycles).

2.3.3. Oxygen reduction reaction

The ORR in the absence of methanol was studied via the linear sweep voltammetry (LSV) technique, with the electrolyte saturated with UHP O₂ (Infra) from the open circuit potential (OCP) to 0.0 V/NHE at 5 mV s⁻¹ and the rotation rates ranged from 100 to 900 rpm as Ru synthesized also by microwave [22]. After these LSV recordings, the electrolyte was saturated again with UHP N₂ (Infra) and then absolute methanol (J T Baker) was added to the electrolyte to reach a final CH₃OH concentration of 2.0 mol l⁻¹, then CV recordings were performed again (15 cycles). Another set of recordings were traced in LSV mode (in the same conditions) for ORR in electrolyte previously saturated with O₂ in the presence of methanol.

2.3.4. Hydrogen oxidation reaction

The hydrogen oxidation reaction was also studied with the linear sweep voltammetry (LSV) technique, but the electrolyte was saturated with UHP H₂ (Infra) from the OCP to 0.320 V/NHE at 3 mV s⁻¹. The rotation rates are also ranged from 100 to 900 rpm.

3. Results and discussion

3.1. Structural and morphological characterization

Figure 1 shows the XRD patterns of RuFe-1 (a) and RuFe-2 (b) electrocatalysts. It can be observed that both materials show two phases: metallic Ru and Fe₂O₃ (Hematite), with similar lattice parameters (based on refinement data, table 1); an amorphous phase (between 2θ = 20°–30°); and wide Ruthenium signals, which are related to the presence of Ru particles in the nano-scale [23, 24]. On the other hand, only the XRD pattern of RuFe-2 shows another phase which is associated with Fe(OH)₃·H₂O₃ₓ (Bernalite). According to table 1, it could be observed that RuFe-1 has a higher content of Ru wt% than RuFe-2, while RuFe-2 shows a higher content of Fe wt% than RuFe-1, which is expected according with the molar ratios used during the syntheses of the materials. A different grain size for every phase in both materials is also noticeable. Where the electrocatalyst with a higher Fe wt% (RuFe-2) shows a higher grain size for every phase. The calculated particle size is consistent with the wide signals observed in the XRD patterns. Data reported by Yassine El Mendili for the Fe₂O₃ phase are used [25], while William D. Birch’s data are used for the Fe(OH)₃·H₂O₃ₓ phase [26] and, similarly, Wyckoof’s data for the Ru phase [27], were used to accomplished the Rietveld refinement. The parameters’ refinement was done in the next order: (1) scale factor and background (with type 1 in the program), (2) lattice parameters, (3) phase.
fractions, (4) profile (with type 2 in the program) and (5) positions and thermal coefficients. The results obtained from Rietveld refinement are also shown in table 1.

The presence of metallic ruthenium can be explained by the thermal decarbonylation of Ru3(CO)12 (equation (7)):

\[
\text{Ru}_3(\text{CO})_{12} \rightarrow 3\text{Ru} + 12\text{CO}
\]  

(7)

The formation of the bernalite and Fe2O3 phases could involve at least two reactions (equations (8) and (9)):

\[
\text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{HCl}
\]

(8)

\[
2\text{Fe(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}
\]

(9)

Figure 2 shows the scanning electron micrographs of Ru-Fe electrocatalysts at two magnifications: 20 000 × and 100 000 ×. A laminar structure with granulated zones for RuFe-1 electrocatalyst (figures 2(a1) and (a2)) is observed, while for RuFe-2 electrocatalyst a sponge-like morphology is observed (figures 2(b1) and (b2)). It is also observed structures with a worm form for RuFe-1, formed by spherical particles joined together with different long and distribution. While RuFe-2 electrocatalyst shows the presence of aleatory spherical particles. Apparently, the amount of iron in the electrocatalyst determines the morphology, size and distribution of the particles. According to the electrochemical characterization shown below, RuFe-1 shows higher current densities than RuFe-2, which could be explained in terms of a possible larger surface area: RuFe-1 (6.85 nm) has a smaller grain size than RuFe-2 (22.97 nm).

3.2. Electrochemical characterization

3.2.1. Cyclic voltammetry

Figure 3 shows the cyclic voltammograms of (a) RuFe-1 and (b) RuFe-2. The CV’s show the first and the thirtieth cycle obtained in the absence of methanol, along with the fifteenth cycle in the presence of methanol 2.0 mol l⁻¹ (as described in the experimental section). In both plots, the current associated with the Vulcan® XC-72 support is subtracted from their respective experimental data. For both materials at the first cycle a pair of redox peaks between 0.6 and 0.8 V/NHE can be observed, which are related to the iron redox couple (Eₙ/ₚ(Fe) = 0.68 V/NHE in 0.5 mol l⁻¹ H₂SO₄) [28, 29]. However, these peaks are less resolved for the material with a lower Fe wt% (or higher Ru wt%, RuFe-1) and they become less intense upon increasing the number of cycles (30th). The Fe redox peaks are not well resolved due to the higher capacitive current densities exhibited by the higher content of Ru in the material, this behavior is observed for materials based only in Ru [6]; and to the possible dissolution of Fe in an acid medium [30]. An opposite behavior is observed in the material with a higher Fe wt% (or lower Ru wt%, RuFe-2), where the intensity of peaks does not decrease significantly upon increasing the number of cycles (30th). Because of the peak-to-peak separations (ΔEₚ = 0.050 V and 0.100 V for RuFe-1 and RuFe-2, respectively) and the current density ratios (jp,r/jp,c = 1.9 and 1.6 for RuFe-1 and RuFe-2, respectively), as there is a transfer of 2 electrons this parameters do not correspond to a fast reversible system, the iron electrochemical process could be considered quasi-reversible on these materials [31].

A small but broad reduction peak is also observed between 0.15 and 0.45 V/NHE for both materials, which is related to the reduction of an oxygen-containing layer on the ruthenium surface formed and grown during the anodic sweep [32]. On the other hand, the hydrogen adsorption and desorption (0.0–0.1 V/NHE) regions are
| Material | Phase          | Lattice parameters                      | Wt%   | Calculated grain size$^\text{(nm)}$ |
|----------|----------------|-----------------------------------------|-------|---------------------------------|
| RuFe-1   | Fe$_2$O$_3$    | $a = 5.0347\ \text{Å}, b = 5.0347\ \text{Å}, c = 13.7581\ \text{Å}, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ$ | 25.66%| 53.03                           |
| Ru       | $a = 2.7096\ \text{Å}, b = 2.7096\ \text{Å}, c = 4.2846\ \text{Å}, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ$ | 74.34%| 6.85                            |
| RuFe-2   | Fe$_2$O$_3$    | $a = 5.0396\ \text{Å}, b = 5.0396\ \text{Å}, c = 13.7829\ \text{Å}, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ$ | 63.96%| 72.38                           |
| Fe(OH)$_x$(H$_2$O)$_x$ | $a = 7.7637\ \text{Å}, b = 7.7578\ \text{Å}, c = 7.7811\ \text{Å}, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 90^\circ$ | 19.31%| 179.94                          |
| Ru       | $a = 2.7106\ \text{Å}, b = 2.7106\ \text{Å}, c = 4.2809\ \text{Å}, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ$ | 16.73%| 22.97                           |

$^\text{a}$ The grain size was obtained from Scherrer equation with LX parameter obtained from the Rietveld Refinement.
observed in both electrocatalysts. In general, the current densities are higher for the material with higher Ru content and with smaller grain size (RuFe-1). Another important feature is that methanol oxidation peaks are not observed (0.8–1.0 V/NHE), i.e., these materials do not show activity towards that reaction.

3.2.2. Oxygen reduction reaction in the absence or presence of methanol

Figure 4 shows the polarization curves of the molecular ORR in 0.5 mol l\(^{-1}\) H\(_2\)SO\(_4\) by (a) RuFe-1 and (b) RuFe-2, in the absence or presence of 2.0 mol l\(^{-1}\) CH\(_3\)OH. Both electrocatalysts show two well-defined regions for the ORR: the kinetic or activation control zone and the mixed control zone. However, the diffusional plateaus in the mass-transfer zone are slightly affected by the reduction of the ruthenium-oxide film [6]; according to figure 3, this process starts at ~0.45 V/NHE. On the other hand, both materials show similar open circuit potentials (table 2) and, similarly to the cyclic voltammetry studies, RuFe-1 shows higher current densities than RuFe-2. The polarization curves are not affected by the presence of methanol during the ORR, thus confirming the tolerance of RuFe electrocatalysts to up to 2.0 mol l\(^{-1}\) CH\(_3\)OH.
According to the Koutecky-Levich equation (equation (10)), the kinetic ($i_k$) and mass transport-controlled ($i_L$) currents combine to yield the total current ($i$) as the sum of reciprocal currents [33]:

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_L}
\]

(10)

Since $i_L$ is given by

\[
i_L = 200nFAC_{O_2}D_{O_2}^{2/3}ν^{-1/6}ω^{1/2} = B_L \cdot ω^{1/2}
\]

(11)

Equation (10) can be rewritten as:

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B_L \cdot ω^{1/2}} = \frac{1}{i_k} + \frac{B_{KL}}{B_L} \cdot ω^{-1/2}
\]

(12)

where $B_{KL} = B_L^{-1}$, 200 is a constant used when the electrode rotation velocity ($ω$) is expressed in rpm and the current in mA, $n$ is the number of electrons involved during the ORR, $A$ is the geometric area (0.1963 cm$^2$), $F$ is the Faraday constant (96485 C mol$^{-1}$), $C_{O_2}$ is the $O_2$ concentration in the bulk of the electrolyte ($1.10 \times 10^{-6}$ mol cm$^{-3}$), $D_{O_2}$ is the $O_2$ diffusion coefficient ($1.40 \times 10^{-5}$ cm$^2$ s$^{-1}$) and $ν$ is the kinematic viscosity of the electrolyte (0.5 mol $L^{-1}$ H$2$SO$_4$ (0.01 cm$^2$ s$^{-1}$)); $B_L$ and $B_{KL}$ are the Levich and Koutecky-Levich slopes of equations (11) and (12), respectively. Figure 5 shows the theoretical (2- and 4- electrons) and experimental Koutecky-Levich plots (at 0.25 V/NHE) for (a) RuFe-1 and (b) RuFe-2, in the absence or presence of 2.0 mol $L^{-1}$ CH$_3$OH. It is considered that electrocatalysts carrying out the ORR by the direct route (equation (1)) are more efficient and therefore they are of most interest for technological applications. The experimental plots show slopes slightly deviated from those calculated for a four-electron process; this suggests that synthesized materials could carry out the ORR by a direct route (equation (1)).

On the other hand, equation (12) is used to study the electrode kinetics. The kinetic current could be obtained by extrapolating an $i$ versus $ω^{-1/2}$ plot, where the limiting current approaches to the infinity and the current would be controlled only by the charge transfer. However, the measured current is smaller than the kinetic-controlled current, because the concentration at the surface is lower than in the bulk. Thus, a correction for mass transport limitation must be done. Equation (13) is used to correct the mass transfer effect to get the $i_k$ value [5–7, 9, 33].

### Table 2. Open circuit potentials and ORR kinetic parameter values of RuFe electrocatalysts in O$_2$-saturated H$_2$SO$_4$ (0.5 mol $L^{-1}$) medium. Reported Pt/Vulcan® and Ru$_x$Fe$_y$ parameters are incorporated as comparison.

| Electro catalyst | [CH$_3$OH] mol$L^{-1}$ | $E^{02}V/NHE$ | b $V$ decade$^{-1}$ | $α$ | $j_0$ mA cm$^{-2}$ |
|------------------|------------------------|--------------|------------------|-----|------------------|
| RuFe-1           | 0.0                    | 0.772        | 0.267            | 0.22 | 1.7 E-03         |
|                  | 2.0                    | 0.774        | 0.270            | 0.22 | 2.0 E-03         |
| RuFe-2           | 0.0                    | 0.775        | 0.322            | 0.18 | 3.6 E-03         |
|                  | 2.0                    | 0.781        | 0.325            | 0.18 | 4.2 E-03         |
| Ru$_x$Fe$_y$ (Reflexing) | 0.0 | Not reported | 0.140 | 0.42 | 2.7 E-05 |
| Ru$_x$Fe$_y$ (Mechanical Milling) | 0.0 | 0.810 | 0.120 | 0.47 | 5.1 E-05 |
| 30% Pt/Vulcan®   | 0.0                    | 1.006        | 0.091            | 0.65 | 2.2 E-04         |

Figure 4. ORR rotating disk electrode current–potential curves in the (-) absence or (+) presence of 2.0 mol $L^{-1}$ CH$_3$OH of (a) RuFe-1 and (b) RuFe-2 electrocatalysts. The electrolyte was 0.5 mol $L^{-1}$ H$_2$SO$_4$ and the sweep rate 5 mV s$^{-1}$. 
This kinetic current ($i_k$) is used to obtain the Tafel curves ($\log i_k$ versus $E$). Critical kinetic parameters are obtained from these curves: the Tafel slope ($b$), the transfer coefficient ($\alpha$) and the exchange-current density ($j_0$). Figure 6 shows the ORR mass-corrected Tafel plots of (a) RuFe-1 and (b) RuFe-2 electrocatalysts, in the (●) absence or (Δ) presence of 2.0 mol l$^{-1}$ CH$_3$OH; Table 2 condenses the kinetic parameters of RuFe electrocatalysts obtained from Tafel plots and the open circuit potentials ($E_{\text{OCP}}$). These parameters are compared with the Pt/Vulcan® electrocatalyst [22] and with Ru$_x$Fe$_y$ electrocatalysts synthesized by conventional methods reported in the literature, such as refluxing [34] and mechanical milling [35].

The Tafel slope is directly linked to the oxygen reduction mechanism, and a value of 120 mV decade$^{-1}$ has been associated with the transfer of a single electron and identified as the rate-determining step of the reaction [5]. However, it could be observed that both electrocatalysts show Tafel slopes higher than 120 mV decade$^{-1}$. According to Atta [36], this behavior could be explained by the presence of a thin layer of a metallic oxide, in this case, by the presence of iron oxide in both electrocatalysts. The transfer coefficient ($\alpha$) is related to the free energy of activation of the process under study; higher values mean smaller activation energies. As with the Tafel slope ($b = \frac{2.303RT}{\alpha nF}$), $\alpha$ is affected by the presence of metallic oxides, yielding values below 0.25. Finally, the exchange-current density ($j_0$, represents the rate at which the electrochemical reaction proceeds back and forth at the equilibrium when the net reaction rate, observed as current flowing through the external circuit, is zero) obtained for both materials are also affected by the presence of metallic oxides; for that reason, the $j_0$ values obtained are even higher than those reported for Pt/Vulcan®. The $j_0$ values have been kept in Table 2 only as a reference.

According to Table 2, the RuFe electrokinetic parameters reported in this work differ from those reported in the literature for Ru$_x$Fe$_y$ electrocatalysts. Previous results reported only the formation of metallic Ru and α-Fe phases using a mechanical milling synthesis method, and nanoparticles of Ru$_x$Fe$_y$ by a refluxing synthesis.
method, with no formation of metallic oxides. As we mentioned above, iron oxide ($\text{Fe}_2\text{O}_3$) is formed by the microwave-assisted synthesis method used in this work, and it could cause an increase in the Tafel slope values, affecting the other electrokinetic parameters ($j_0$ and $\alpha$). On the other hand, open circuit potentials of the RuFe-1 and RuFe-2 electrocatalysts are only slightly lower than for Ru$_x$Fe$_y$.

**Figure 7.** HOR rotating disk electrode current–potential curves of (a) RuFe-1 and (b) RuFe-2 electrocatalysts. The electrolyte was 0.5 mol l$^{-1}$ H$_2$SO$_4$ and the sweep rate 3 mV s$^{-1}$.

**Figure 8.** Theoretical (2 e$^-$) and experimental Koutecky-Levich plots (at 0.14 V/NHE) of (▲) RuFe-1 and (△) RuFe-2 electrocatalysts.

**Table 3.** Open circuit potentials and HOR kinetic parameters values of RuFe electrocatalysts in H$_2$-saturated H$_2$SO$_4$ (0.5 mol l$^{-1}$) medium. The parameters are compared with Ruthenium electrocatalysts reported in the literature.

| Electro catalyst | $E_{\text{H}_2}^{\text{RHE}}$ V/NHE | $b$ mV Decade$^{-1}$ | $1-\alpha$ | $j_0$ mA cm$^{-2}$ |
|------------------|------------------|------------------|------------------|------------------|
| RuFe-1           | 0.0              | 123              | 0.48            | 0.57            |
| RuFe-2           | 0.0              | 118              | 0.50            | 0.55            |
| Ru-DCB$^{[37]}$  | 0.0              | 40.8             | 0.55            | 0.29            |
| Ru-ETG$^{[37]}$  | 0.0              | 39.1             | 0.49            | 0.32            |
| Ru-H$_2$O$^{[18]}$ | 0.0              | 49.2             | 0.60            | 0.11            |

* DCB = dichlorobenzene, ETG = ethylene glycol.
3.2.3. Hydrogen oxidation reaction

Figure 7 shows the LSV’s for the HOR of (a) RuFe-1 and (b) RuFe-2. It can be observed that both materials carry out the HOR with OCP values equal to 0 V/NHE (table 3), i.e., the expected thermodynamic potential value. On the other hand, the theoretical (2-electrons) and experimental Koutecky-Levich (K-L) plots obtained from figure 7 at 0.14 V/NHE are shown in figure 8. As expected, both materials show experimental K-L slopes similar to the theoretical values.

The HOR kinetic parameters are estimated from their corresponding mass-corrected Tafel plots (figure 9). These parameters are shown in table 3 along with those of metallic Ru electrocatalysts reported in the literature, synthesized by a microwave-assisted process using water [18] and two different organic solvents (dichlorobenzene and ethylene glycol) [37]. There is no information previously reported on HOR for the RuFe-type electrocatalysts. It can be observed that both RuFe-1 and RuFe-2 electrocatalysts show Tafel slopes ($\approx$0.120 V decade $^{-1}$) associated with a Tafel/Volmer mechanism, as per equations (4) and (6), respectively [5]. The HOR mechanism is completely different for metallic Ru reported in the literature, where a Heyrovsky/Volmer mechanism is observed ($\approx$0.040 V decade $^{-1}$); this behavior could be associated to the presence of iron oxide. On the other hand, the $\alpha$ values are similar for all electrocatalysts. Another important feature is that RuFe electrocatalysts show slightly higher $j_0$ values than Ru reported in the literature.

4. Conclusion

RuFe electrocatalysts were synthesized using a green chemistry method by a microwave-assisted process in deionized water, thereby avoiding the use of organic solvents as reaction media and long synthesis times used by conventional methods. The electrochemical activities of the electrocatalysts synthesized are improved because they can perform both the ORR (with tolerance to the presence of 2 mol $1^{-1}$ methanol) and the HOR, as opposed to the RuFe electrocatalysts reported in the literature, where only the ORR studies are shown. Therefore, the RuFe electrocatalysts reported in this work could be used as anode and cathode in a PEMFC and DMFC.

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ORCID iDs

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