Microwave assisted synthesis of metallic Ru for the HOR and ORR

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Abstract
Metallic ruthenium electrocatalyst with activity for the hydrogen oxidation reaction and the oxygen reduction reaction has been synthesized by microwave irradiation at 180 °C in deionized water as reaction media. Characterization of the material by ATR-FTIR spectroscopy shows a complete decarbonylation of the precursor Ru3(CO)12 with formation of metallic Ru, which is confirmed by the corresponding x-ray diffraction analysis. Evaluation of the material’s electrocatalytic properties by the rotating disk electrode technique in 0.5 mol l−1 allows the study of hydrogen oxidation and oxygen reduction reaction using linear sweep voltammetry, exhibiting that the diffusional processes of H2 and O2 can be improved by modifying the electrocatalytic ink preparation.

1. Introduction

A fuel cell is an electrochemical device that converts the chemical energy of a fuel directly into electricity without any intermediate thermal or mechanical processes, it operates without pollution when run on pure hydrogen, having only water and heat as by-products. Its applications are vastly diverse such as [1]: stationary electric power (from 1 to 10 MW), distributed generation or small modular power (∼30 MW), vehicle motive power (from 50 to 100 kW), space and other closed environment power (1 kW PEFC in the Gemini program and 1.5 kW AFC in the Apollo program), auxiliary power systems (automotive propulsion and distributed power generation, from 1 to 15 kW).

Proton exchange membrane fuel cells (PEMFC) are galvanic cells which consist of an anode (electrode at which oxidation takes place) and cathode (electrode at which reduction takes place) separated by an electrolyte; hydrogen is supplied at the anode and oxygen at the cathode. These electrodes are most commonly composed by platinum catalyst to increase the rate at which the chemical reaction occurs [2]. However, Pt is very expensive ($50 g−1) [3], so the catalyst loading (10–20 μg-Pt cm−2) [4] is a significant factor in the cost of a fuel cell. While the anodic process of the hydrogen oxidation reaction (HOR) occurs relatively fast and with a negligible overpotential loss when using pure hydrogen, at the cathode, the mechanism for the oxygen reduction reaction (ORR) is very complex; it requires to break a strong O–O bond early by a direct 4–electron mechanism, which is the desired pathway to minimize higher over-potentials (∼0.300 V) at low current densities. Nevertheless, ORR can proceed by a 2–electron mechanism too, when this process takes place, the open circuit potential (OCP) is lowered with respect to the thermodynamic potential due to the production of peroxide as an intermediate. In this way, the ORR mechanism contributes to a lowering of the catalytic activity even on Pt (10−10 to 10−12 A cm−2) [5]. On the other hand, another limiting factor of the PEMFC is when the H2 provided at the anode, is produced by steam reforming, in which CO is present at ppm levels, which binds very strong to Pt electrocatalyst, resulting in a decrease on its activity, consequently requiring a much higher anode potential to sustain the rate of hydrogen electrooxidation [6].

In this way, to improve the activity of Pt toward ORR and HOR, Pt-based alloy (Pt-Fe, Pt-Co, Pt-Ni, Pt-Cu, Pt-Ru) [7, 8], binary PtMx (M=Cu, CO, Ni) and ternary PtNi3M (M = Cu, Co, Fe, Cr) [9] electrocatalysts have...
been investigated; furthermore Pt-free materials such as Ru [8, 10], Ru-based bimetallic electrocatalysts (RuTiNx, RuCrNx, RuFeNx, RuCoNx and RuPbNx) [11], W and Ag-based materials [12] have been studied. However, these kinds of materials have been synthesized using conventional methods, i.e., by refluxing conditions, solid state–process, impregnation/freeze-drying route, reduction reaction, among others [7, 9, 11]. But some of these heating treatments are slow and inefficient methods for transferring energy into the system, so these processes can take hours, besides that organic solvents (refluxing method) must be used. In contrast, microwave irradiation produces efficient internal heating by direct coupling of microwave energy with ions or polar molecules that are present in the reaction mixture; adding the advantage that in pressurized reaction vessels, the boiling points of solvents become a less important factor, i.e., low boiling point solvents that are normally ignored at high temperature syntheses, such as H2O, can be used. Bringing the possibility of use water, which is a polar microwave absorber solvent, that has friendly environmental properties as it is nontoxic, noncorrosive, nonflammable, and has relatively low vapor pressure as compared to organic solvents [13].

Recently there has been an interest in synthesizing electrocatalysts for PMFCs using a microwave thermal treatment. For example, PtRu/Carbon nanocomposite as anode in a direct methanol fuel cell (DMFC) [14]; CoSe [15], Ru [16], Os [17] and CoFeRu [18] electrocatalysts for the ORR; and Ru for the HOR [19] have been reported, but the use of organic solvents as reaction media remains. On the other hand, Sandoval et al have reported the synthesis of CoFeRu electrocatalyst using an organic solvent [18] compared with H2O [20] as microwave absorbing media, and they found a better electrocatalytic behavior for the ORR when the material is synthesized using H2O.

In this way, this article reports the synthesis of metallic Ru electrocatalyst by a green microwave-assisted method, i.e., using deionized water as reaction media, with short synthesis times (30 min). Moreover, shows the materials electrochemical evaluation for both the hydrogen oxidation reaction and the oxygen reduction reaction (in the absence or presence of methanol).

2. Experimental details

2.1. Synthesis and characterization of Ru catalyst
The metallic ruthenium electrocatalyst was synthesized using 80 mg of triruthenium dodecacarbonyl [99% Ru3(CO)12, Aldrich], which was mixed with 10 ml of deionized water (18.2 MΩ cm). The mixture was deposit in a polytetrafluoroethylene (PTFE) tube and then treated thermally using an Anton Paar Synthos-3000 Microwave Oven, experimental conditions are shown in table 1. The black powders obtained were washed with deionized water and dried at room temperature.

The ruthenium electrocatalyst was characterized by attenuated total reflection-infrared spectroscopy (ATR-FTIR), on a Thermo Scientific ATR-FTIR spectrometer; and by x-ray diffraction, on a Rigaku D/max-2100 diffractometer (Cu Kα1 radiation, 1.5406 Å).

2.2. Electrochemical experiments

2.2.1. Electrode preparation
Three different inks were prepared by mixing always 2 mg of 30 wt% Ru/Vulcan® XC-72 (Cabot) with different amounts of Nafion® solution (5 wt% in lower aliphatic alcohols, Electrochem) and isopropyl alcohol (J.T. Baker, 99.90%). The first ink (ink-a), which was used for both the hydrogen oxidation and oxygen reduction studies, contains only 15 μl of Nafion; while ink-b (used only for HOR study) was prepared by adding 10 μl of Nafion® and 90 μl of isopropyl alcohol, and the third one, ink-c (used only for ORR study) with 20 μl of Nafion® and 20 μl of isopropyl alcohol. All the mixtures were sonicated for 10 min on a Cole-Palmer sonicator and deposited on the glassy carbon (GC) disk electrode, previously polished on a MicroCloth polishing cloth with alumina abrasive (5 and 0.3 μm), and cleaned by ultrasonication in deionized water (geometrical surface area = 0.1963 cm²) and dried at room temperature. 5 μl of the resulting ink-a and 10 μl of the resulting inks b and c were deposited on the GC electrode, respectively. Electrocatalyst and Nafion® loadings (μg cm⁻²) for each ink is showed in table 2.

Table 1. Experimental conditions for microwave-assisted synthesis of metallic Ru.

| Step | Program | Temperature °C | Time minutes:seconds | Stirrer |
|------|---------|----------------|-----------------------|--------|
| 1    | Heat to temperature | 180 | 15:00 | on |
| 2    | Hold | 180 | 30:00 | on |
| 3    | Cool down | 30 | 30:00 | on |
Table 2. Electrocatalyst and Nafion® loadings for each ink prepared.

| Ink | Electrocatalyst (μg cm⁻²) | Nafion® (μg cm⁻²) |
|-----|--------------------------|-----------------|
| a   | 1 020                    | 1 200           |
| b   | 300                      | 240             |
| c   | 760                      | 1 200           |

2.2.2. Equipment

The electrochemical studies were carried out at room temperature in a conventional electrochemical cell with three electrodes: working (electrocatalytic ink), counter (graphite rod) and reference (Hg/Hg₂SO₄/0.5 mol l⁻¹ H₂SO₄; 0.68 V/NHE). The potentials are referred to normal hydrogen electrode (NHE). The electrolyte used (0.5 mol l⁻¹ H₂SO₄) is prepared with 98% sulfuric acid (J.T. Baker) and deionized water (18.2 MΩ cm). The glassy carbon disk electrode was operated with a speed control unit (AMETEK, 616A) and used for the rotating disk electrode (RDE) studies. Electrochemical data was acquired by a potentiostat/galvanostat (PINE AFCBP1) commanded by AfterMath® software.

2.2.3. Hydrogen oxidation reaction

Before carrying out the HOR, the electrolyte was saturated with N₂ (Infra, UHP) and then the electrode surfaces using inks a and b, respectively, were activated by cyclic voltammetry (CV) technique, scanning from 0 to 0.98 V/NHE at 20 mV s⁻¹ (30 cycles), until no variations were observed. Once the electrode surface had been activated, the hydrogen oxidation reaction was studied for both inks by linear sweep voltammetry (LSV) technique, with the electrolyte saturated with H₂ (Infra, UHP) from the open circuit potential (OCP) to 0.30 V/NHE at 5 mV s⁻¹.

2.2.4. Oxygen reduction reaction

The ORR in the absence and presence of methanol was also studied by LSV technique, but with the electrolyte saturated with O₂ (Infra, UHP) from the open circuit potential (OCP) to 0.0 V/NHE at 5 mV s⁻¹. This study was performed for inks a and c, respectively. However, only ink-a was activated with CV technique before carrying out the ORR. To avoid the formation of ruthenium oxides on the surface, CV was not performed on ink-c. For ORR studies in the presence of methanol, absolute methanol (J.T. Baker) was added to the electrolyte to reach a final CH₃OH concentration of 2.0 mol l⁻¹.

The rotation rates ranged only from 100 to 600 rpm for ink (a), because the diffusional plateaus in the mass-transfer zone during HOR and ORR experiments shows a poor definition; while for inks b and c, where the diffusional plateaus are defined, rotational rates were from 100 to 1600 rpm.

3. Results and discussion

3.1. Structural characterization

Figure 1 shows the ATR-FTIR spectra of the precursor Ru₃(CO)₁₂ and the ruthenium electrocatalyst synthesized at 180 °C by MW irradiation. Carbonyl stretching bands (υ(CO)) for Ru₃(CO)₁₂ has been reported around 2150–1950 cm⁻¹ [21], this very strong band is observed in the precursor; however, it disappears after precursor is heated by microwave treatment, i.e., a decarbonylation of the precursor could be carried out with a possible formation of metallic Ru. This fact is confirmed by the corresponding x-ray diffraction pattern (figure 2), where according to the international tables for crystallography [22], the diffraction peaks of synthetic metallic ruthenium match with those observed for Ru electrocatalyst synthesized. The grain size obtained by Scherrer formula (11.1 nm) is in agreement with those reported for Ru synthesis using organic solvents as microwave absorber [19], remarking nanoparticle formation as another property of microwave-assisted synthesis. Table S1 is available online at stacks.iop.org/MRX/7/025503/mmedia shows the lattice parameters and another crystallographic information.

3.2. Electrochemical characterization

3.2.1. Hydrogen oxidation reaction

Figure 3 shows the cyclic voltammograms of metallic Ru for inks a (–) and b (–), respectively. Here can be observed for both Ru-inks a hydrogen region over the potential range from 0.10 to 0.00 V/NHE; while the surface oxidation of Ru occurs very early at ~0.20 V/NHE, showing two anodic peaks at ~0.40 and 0.60 V/NHE (less intense for ink-b); finally the reduction of the ruthenium oxide film starts at ~0.60 V/NHE, with a cathodic
peak at ∼0.30 V/NHE. These CV profiles are in agreement with that reported for Ruthenium electrodes [23] and by Pt electrodes plated with Ru [24]. Additionally, figure 4 shows the linear sweep voltammograms for the hydrogen oxidation reaction for both inks. Where for ink-a (−), the diffusional plateaus at different rpms in the mass-transfer zone are not well defined, this effect could be due to an excess of Na® solution (1 200 μg cm−2) and a high electrocatalyst loading (1 020 μg cm−2), forming a thick film causing an inefficient diffusion of hydrogen in the catalyst layer [25, 26]. When the loadings of Na® (240 μg cm−2) and electrocatalyst (300 μg cm−2) are lowered (ink-b (−)), the three regions for the HOR are well defined: the kinetic or activation control zone, the mixed control region and the mass transfer zone. It can be also observed that the open circuit potential (table 3) is slightly improved (∼10 mV) when the loadings of Na® and catalyst are lowered.

The kinetic parameters (table 3) obtained from mass corrected Tafel plots (figure 5), were calculated only for ink-b because ink-a does not have well-defined diffusion plateaus for a proper data processing. These parameters are compared with Ru electrocatalyst synthesized using organic solvents as microwave absorbant. The Tafel slopes (b) obtained are in agreement with the theoretical prediction for the Heyrovsky (equation (1))/Volmer (equation (2)) mechanism, with the Volmer reaction as the rate determining step [27].

\[
H_2 + M \rightleftharpoons MH_{ads} + H^+ + e^- \tag{1}
\]

\[
MH_{ads} \rightleftharpoons M + H^+ + e^- \tag{2}
\]

The exchange current density (j0) is a parameter that is proportional to the rate constant (k) of the reaction (HOR). Results show that j0 values have the same order of magnitude for all electrocatalysts. On the other hand,
Figure 3. Cyclic voltammograms for ink-a (–) and ink-b (–) in 0.5 mol l\(^{-1}\) H\(_2\)SO\(_4\) as the electrolyte obtained at a sweep rate of 20 mV s\(^{-1}\).

Figure 4. Hydrogen oxidation reaction studies for ink-a (–) and ink-b (–). The electrolyte was 0.5 mol l\(^{-1}\) H\(_2\)SO\(_4\) and the sweep rate was 5 mV s\(^{-1}\).

Table 3. Open circuit potentials (E\(_{OC}\)) and electrokinetic parameters for both ink-b and for Ru reported in the literature \[19\] as comparison.

| Electrocatalyst | E\(_{OC}\) (V/ NHE) | b (mV decade\(^{-1}\)) | (1-\(\alpha\)) | \(j_0\) (mA cm\(^{-2}\)) |
|----------------|---------------------|------------------------|----------------|----------------------|
| Ru ink-b       | 0.0                 | 49.2                   | 0.601          | 0.113                |
| Ru-ETG\(^a\)   | 0.0                 | 39.1                   | 0.492          | 0.321                |
| Ry-DCB\(^a\)   | 0.0                 | 40.8                   | 0.549          | 0.291                |

\(^a\) ETG = ethylene glycol; DCB: dichlorobenzene.
although the \((1-\alpha)\) value for ink-b is relatively high, it is expected according to Gileadi \[28\], that it takes values greater than unity for a multi-step reaction.

3.2.2. Oxygen reduction reaction

Cyclic voltammograms in absence \((-\)) and presence \((-\)) of 2.0 mol l\(^{-1}\) methanol for ink-a are shown in figure 6. The CV profiles are the same as those explained for figure 4. However, an important feature is observed, methanol oxidation peaks are not present \[16\], which means that the material does not show activity toward that reaction.

Figure 7 shows the linear sweep voltammograms for the oxygen reduction reaction for (a) ink-a and (b) ink-c, in absence \((-\)) and presence \((-\)) of methanol. It can be observed for ink-a an important interference in the mass-transfer zone due to the presence of the reduction of ruthenium oxide film \((\text{at ca. 0.6 V/NHE})\) formed during CV studies, hence the diffusional plateaus are not well defined, this intense cathodic peak is observed in CV studies (figure 6). Similar effect for Ru electrocatalyst synthesized by microwave method using 1,2-dichlorobenzene as solvent \[16\], and by pyrolysis \[10\] in \(\text{N}_2\) atmosphere at 140 °C and in \(\text{N}_2/\text{H}_2\) atmosphere at 360 °C is also observed. On the other hand, it can be observed for ink-c that the effect of formation of metallic oxide in the mass-transfer zone is reduced when the loading of catalyst is diminished and CV is not performed before LSV studies, i.e., the diffusion of oxygen toward the catalyst layer is improved. Another important feature is

![Figure 5](image1.png)

**Figure 5.** Mass corrected Tafel plots for ink-b.

![Figure 6](image2.png)

**Figure 6.** Cyclic voltammograms in the absence \((-\)) and presence \((-\)) of 2.0 mol l\(^{-1}\) methanol for ink-a. The electrolyte was 0.5 mol l\(^{-1}\) \(\text{H}_2\text{SO}_4\) and the sweep rate was 20 mV s\(^{-1}\).
shown for both inks, the LSVs are practically unchanged by the presence of methanol, i.e., the electrocatalyst is tolerant to the presence of CH₃OH during the ORR.

Finally, the mass transport corrected Tafel plot for the oxygen reduction reaction (figure 8) obtained from LSVs studies (figure 7(b)) is constructed (only for ink-c) according to the literature [29]. In this way, table 4 summarizes the OCPs and the electrokinetic parameters for metallic Ru synthesized in H₂O and for Ru electrocatalysts synthesized in 1,2-dichlorobenzene by MW irradiation* and by refluxing** as comparison (the kinetic parameters, as for HOR studies, were not calculated for ink-a). The OCPs

Table 4. Open circuit potentials (E_OC) and electrokinetic parameters for ink-c. Ru electrocatalysts synthesized in 1,2-dichlorobenzene by MW irradiation* and by refluxing** are also included as comparison.

| Electro catalyst | [CH₃OH] (mol l⁻¹) | E_OC (V/NHE) | b (V decade⁻¹) | α  | j₀ (mA cm⁻²) |
|-----------------|-------------------|--------------|----------------|----|-------------|
| Ru ink-c        | 0                 | 0.820        | 0.144          | 0.405 | 4.8E-05    |
|                 | 2                 | 0.833        | 0.133          | 0.438 | 3.2E-05    |
| Ru-DCB*         | 0                 | 0.851        | 0.155          | 0.383 | 2.7E-04    |
|                 | 2                 | 0.846        | 0.160          | 0.367 | 3.0E-04    |
| Ru-DCB**        | 0                 | 0.763        | 0.181          | 0.326 | 2.1E-04    |
|                 | 2                 | 0.763        | 0.182          | 0.326 | 1.7E-04    |

Figure 7. Linear sweep voltammetry for ORR in the absence (--) and presence (--) of 2.0 mol l⁻¹ methanol for (a) ink-a and (b) ink-c. The electrolyte was 0.5 mol l⁻¹ H₂SO₄ and the sweep rate was 5 mV s⁻¹.

Figure 8. Oxygen reduction reaction mass-transfer corrected Tafel plots in the absence (--) or presence (--) of 2.0 mol l⁻¹ methanol for ink-c.
are similar when Ru electrocatalysts are synthesized by a microwave-assisted method, but it is almost 100 mV lower when it is synthesized by a conventional method, i.e., this parameter is improved.

On the other hand, Tafel slope is a parameter related to the reaction mechanism (ORR), a Tafel slope value of 0.120 V dec$^{-1}$ indicates that the rate-determining step in the oxygen electroreduction reaction corresponds to a single electron transfer. However, it has been reported that a thin layer of oxide on the electrocatalyst surface could cause an increase in the Tafel slope and therefore the rate-determining step would not correspond to a single electron-transfer [30], which also could affect the other electrokinetic parameters, $\alpha$ and $j_0$. In this way, it can be observed that Tafel slope and the charge transfer coefficient are improved with respect to those reported in the literature.

4. Conclusion

Ru electrocatalyst with a grain size of 11.1 nm and with a hexagonal crystal system shows activity for both the hydrogen oxidation reaction and the oxygen reduction reaction. The electrocatalyst was synthesized by a green chemistry process, using water as absorbing microwave solvent. The new formulations for preparing electrocatalytic inks improve the diffusional processes of hydrogen oxidation and oxygen reduction.

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