



## Short communication

# Ruthenium based electrocatalysts for hydrogen oxidation, prepared by a microwave assisted method



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## HIGHLIGHTS

- Ruthenium catalysts synthesized by a microwave-assisted method.
- Ruthenium materials as HOR catalysts.
- Potential use of these materials as PEMFC anodes.

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## ABSTRACT

Ruthenium monometallic electrocatalysts for the hydrogen oxidation reaction (HOR) were prepared by microwave irradiation in *o*-dichlorobenzene and ethylene glycol. The products were characterized structurally by X-ray diffraction and FT-IR spectroscopy; morphologically by scanning electron microscopy and their chemical composition was determined by energy-dispersive spectroscopy analysis. The electrocatalytic properties of the materials were evaluated by rotating disk electrode measurements in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. The kinetic parameters, such as the Tafel slope, exchange current density and charge transfer coefficient, are reported. The ruthenium electrocatalysts show a *dual-path* mechanism in a similar way as platinum.

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## 1. Introduction

The slow kinetics of the oxygen reduction reaction ( $j_o \sim 10^{-10}$ – $10^{-12}$  A cm<sup>-2</sup>) and methanol poisoning at the cathode in a PEMFC and DMFC [1,2], respectively, as well as the CO poisoning at the anode in a PEMFC [3] (showed by platinum electrocatalysts), have resulted in the development of alternative materials to platinum with high activity for the ORR and HOR, but with resistance to the contaminants mentioned above.

Ru-based catalysts are considered a promising alternative to Pt as cathode catalysts in DMFCs (and PEMFCs), due to their tolerance to methanol oxidation. This is attributed to the lack of available surface sites for methanol adsorption due to the strongly adsorbed

oxygenated species [4]. On the other hand, most of the materials reported in the literature for the hydrogen oxidation reaction (HOR) have been based on platinum and their alloys (Pt–Ru, Pt–Mo) [5], Pd alloys (Pd–Au) [6] and more recently, osmium [7]; however, to the best of our knowledge, no ruthenium monometallic catalysts have been studied. Many of such catalysts reported in the literature have been synthesized using a conventional heating method, i.e., organic solvents at their refluxing temperature or by pyrolysis of some metal precursors [8–14]. However, this is a relatively slow and inefficient method for transferring energy into the system because heat passes first through the walls of the vessel in order to reach the solvent and reactants; furthermore, this results in the temperature of the vessel being higher than that of the reaction mixture. On the other hand, microwave energy couples directly with the molecules that are present in the reaction mixture, leading to a rapid rise in temperature; the process is not dependent upon the thermal conductivity of the vessel materials.

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Microwave energy has been employed in many recent chemical reaction studies and has been found to change the kinetics and selectivity, often in favorable ways. These reactions include organic and inorganic syntheses, selective sorption, oxidation/reduction, polymerization, among many other processes [15]. Recently, we have reported [16,17] the use of microwave energy for the synthesis of ruthenium and osmium catalysts for the oxygen reduction reaction (ORR) with an electrochemical behavior similar to that exhibited by materials obtained by a conventional synthesis method. The present article reports on the electrocatalytic activity of Ru materials prepared by a microwave-assisted method for the hydrogen oxidation reaction in an acid medium.

## 2. Experimental

### 2.1. Synthesis of the catalysts

The ruthenium electrocatalysts were synthesized using 0.063 mmol of triruthenium dodecacarbonyl  $[\text{Ru}_3(\text{CO})_{12}]$ , Aldrich), mixed with 5 mL of one of two organic solvents: *o*-dichlorobenzene (b.p. 178–180 °C, Aldrich) and ethylene glycol (b.p. 195–198 °C, Aldrich). The mixture was thermally treated using microwave irradiation on an Anton Paar-Monowave reactor 300; experimental conditions are shown in Table 1. The products obtained were washed with 2-propanol (J.T. Baker) and dried at room temperature. The solvents were selected according to their different ability to absorb microwave energy [15].

### 2.2. Structural characterization of the catalysts

The electrocatalysts synthesized were structurally characterized using reflectance FT-IR spectroscopy on a Perkin–Elmer-GX3 spectrometer, with the samples dissolved in FT-IR grade KBr (Aldrich). For the XRD studies, a Rigaku D/max-2100 diffractometer, with  $\text{Cu K}\alpha 1$  irradiation (1.5406 Å) was used. A Philips XL30ESEM microscope was used to obtain scanning electron micrographs and X-ray energy-dispersive spectra (EDS) of the catalysts, for surface morphology and chemical composition studies, respectively.

### 2.3. Electrochemical experiments

#### 2.3.1. Electrode preparation

The electrode for the rotating disk electrode (RDE) studies was prepared by mixing 1.7 mg of Vulcan<sup>®</sup> XC-72 (Cabot) and 0.3 mg of the catalyst with 10  $\mu\text{L}$  of a 5% Nafion<sup>®</sup> solution (ElectroChem) in an ultrasonic bath; 2  $\mu\text{L}$  of the resulting slurry were deposited on the glassy carbon electrode and dried at room temperature. The cross-sectional area of the disk electrode on which the catalyst-support mixture was deposited (geometrical area) was 0.072  $\text{cm}^2$ .

**Table 1**  
Experimental conditions during the microwave assisted synthesis of  $\text{Ru}_y\text{-ETG}$  and  $\text{Ru}_y\text{-DCB}$ .

Step	Program	Temperature °C	Time minutes:seconds	Stirrer
1	Heat to temperature	180	3:00	On
2	Hold	180	30:00	On
3	Heat to temperature	200	5	On
4	Hold	200	1	On
5	Heat to temperature	250	5	On
6	Hold	250	4	On
7	Cool down	30	–	On

#### 2.3.2. Equipment

The RDE studies were carried out at room temperature, in a conventional electrochemical cell, with a mercury sulfate electrode ( $\text{Hg}/\text{Hg}_2\text{SO}_4/0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ; abbreviated as MSE) as reference ( $\text{MSE} = 0.680 \text{ V/NHE}$ ), which was connected to the cell through a bridge with a Luggin capillary, and a graphite rod as counter electrode. The potentials were referred to normal hydrogen electrode (NHE). The 0.5  $\text{mol L}^{-1} \text{ H}_2\text{SO}_4$  solution used as electrolyte was prepared with 98% sulfuric acid (J.T. Baker) and deionized water (18.2  $\text{M}\Omega\text{-cm}$ ). A potentiostat/galvanostat (Solartron 1287) and a PC with CorreWare software were used for the electrochemical measurements. A Radiometer Analytical BM-EDI101 glassy carbon rotating disk electrode (with a CTV101 speed control unit) was used for the voltammetry studies.

#### 2.3.3. Electrochemical methods

**2.3.3.1. Cyclic voltammetry.** Cyclic voltammetry (CV) experiments were done to clean, activate and characterize the electrode surface of ruthenium materials for the HOR. This was done by scanning (in the electrolyte saturated with nitrogen; Infra, UHP) between 0 and 0.98 V/NHE at 20  $\text{mV s}^{-1}$ , until no variation in the voltammograms was observed (30 cycles).

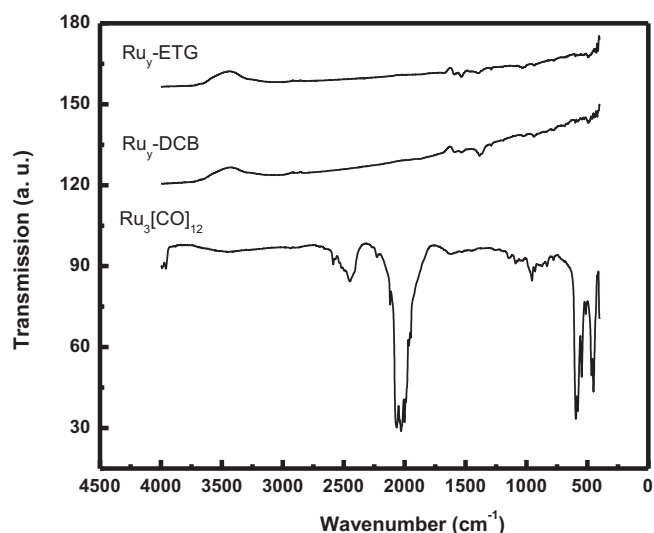
**2.3.3.2. Hydrogen oxidation reaction (HOR).** Linear sweep voltammetry (LSV) was done by saturating the electrolyte with hydrogen (Infra; UHP) for 15 min. Polarization curves were obtained from the open circuit potential in the presence of hydrogen,  $E_{\text{oc}}^{\text{H}_2}$ , to 0.280 V/NHE. The rotation rates ranged from 100 to 900 rpm.

## 3. Results

### 3.1. Structural characterization

Fig. 1 shows the FT-IR spectra of the materials prepared, along with the spectrum of the  $\text{Ru}_3(\text{CO})_{12}$  precursor as reference. The latter shows strong carbonyl stretching vibration bands around 2040  $\text{cm}^{-1}$ , as well as a group of bands around 570  $\text{cm}^{-1}$ , which have been assigned to carbonyl deformation modes,  $\delta_{\text{M-CO}}$  [18]. As for the ruthenium catalysts prepared, they do not show any carbonyl bands, inferring that they virtually lose all these groups.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the materials synthesized and the  $\text{Ru}_3(\text{CO})_{12}$  precursor as reference.



**Fig. 1.** FT-IR spectra of  $\text{Ru}_3(\text{CO})_{12}$  and the ruthenium catalysts synthesized in *o*-dichlorobenzene ( $\text{Ru}_y\text{-DCB}$ ) and ethylene glycol ( $\text{Ru}_y\text{-ETG}$ ).

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