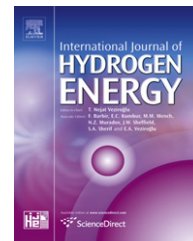


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Microwave assisted synthesis of ruthenium electrocatalysts for oxygen reduction reaction in the presence and absence of aqueous methanol

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ABSTRACT

In this work we present the synthesis of ruthenium based electrocatalysts for oxygen reduction reaction in 0.5 mol L⁻¹ H₂SO₄, using microwave irradiation at different power, time and temperature conditions. Ru₃(CO)₁₂ and 1,2-dichlorobenzene were used as precursor and solvent respectively. The materials obtained were structurally characterized by FT-IR spectroscopy and X-ray diffraction; their chemical composition was determined by energy-dispersive spectroscopy analysis. The rotating disk electrode technique was used for the electrochemical characterization of the catalysts; the oxygen reduction reaction was performed in the presence and absence of aqueous methanol solutions. The electrocatalytic activity towards the oxygen reduction reaction is similar to that of ruthenium catalysts synthesized using a conventional process reported in the literature.

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1. Introduction

The performance of PEM fuel cells is usually limited by the slow oxygen reduction kinetics and the cross-over effect in direct methanol fuel cells. Another important feature is that the oxygen reduction reaction (ORR) must proceed via the overall four-electron transfer to form water. Platinum and platinum alloys have been the most employed electrocatalysts in fuel cells; however, even with these materials the kinetics of the ORR is slow. Furthermore, there is a great interest in the development of alternative materials for this reaction. Transition metal carbonyl clusters have shown a good electrocatalytic activity towards the ORR, with tolerance to the presence of methanol molecules. However, many of these electrocatalysts have been

synthesized using a conventional heating method of the precursor, i.e., using organic solvents at their refluxing temperature with much longer synthesis times (≥ 20 h) [1–11], or by pyrolysis of some metal carbonyl compounds for ≥ 5 h [12,13]. This could be a slow and relatively inefficient method for transferring energy into the system because it depends on convection currents and the thermal conductivity of the various materials that must be penetrated, and generally results in the temperature of the vessel being higher than that of the reaction mixture. This is particularly true if reactions are performed under reflux conditions, whereby the temperature of the bath fluid is typically kept at 10–30 °C above the boiling point of the reaction mixture in order to ensure an efficient reflux. In addition, a temperature gradient can develop within the sample and

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Table 1 – Chemical composition of the ruthenium electrocatalysts determined by EDS experiments (wt %).

Element	180°/80°W/30°min	180°/100°W/30°min	180°/100°W/60°min
Ru	89.05	83.12	74.19
C	9.92	13.01	23.44
O	0.97	4.19	2.38

local overheating can lead to product, substrate or reagent decomposition. In contrast, microwave irradiation produces efficient internal heating by direct coupling of microwave energy with the molecules (solvents, reagents, catalysts) that are present in the reaction mixture. Microwave irradiation, therefore, raises the temperature of the whole volume simultaneously whereas in the conventionally heated vessel, the reaction mixture in contact with the vessel wall is heated first. The very efficient internal heat transfer results in minimized wall effects, which may lead to the observation of the so-called specific microwave effects, for example in the context of diminished catalyst deactivation [14].

Recently, it has been reported the synthesis of catalysts (Pt and Pt alloys) for PEMFC applications using microwave irradiation, mainly as anodes in DMFC [15–17]. These results showed an enhancement on their activity towards methanol oxidation, with current densities higher than that of commercial platinum and platinum alloys. On the other hand, Hong Zhu et al. [18] have reported studies on PtAuSn/C nanoparticles for ethanol electrooxidation, as cathode catalyst in DMFC. Parisa Nekooi et al. [19] synthesized CoSe nanoparticles as an alcohol tolerant oxygen reduction catalyst. Ayse Bayrakceken et al. [20] improved the carbon dioxide tolerance of PEMFC electrocatalyst by using microwave irradiation technique, while Glaspell et al. [21] reported the synthesis of Au and Pd nanoparticle catalysts for CO oxidation. The scope of this study is to further analyze the effect of the presence of methanol on the microwave synthesized ruthenium based oxygen reduction catalysts.

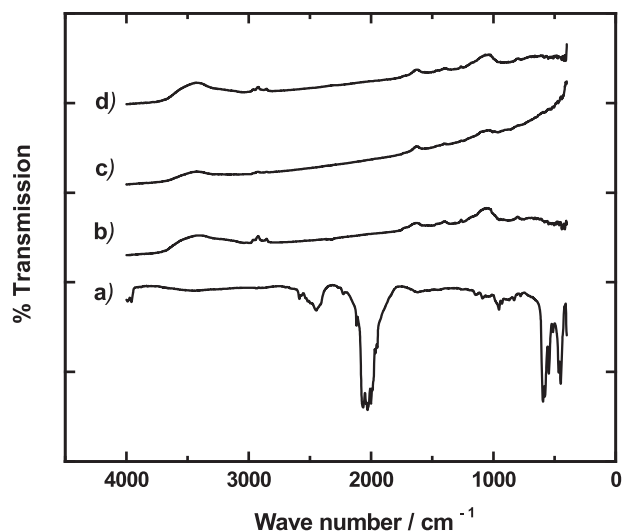


Fig. 1 – FT-IR spectra for a) $\text{Ru}_3(\text{CO})_{12}$ and the ruthenium catalysts synthesized under the following conditions: b) 180 °C/30 min/80 W c) 180 °C/30 min/100 W d) 180 °C/60 min/100 W.

2. Experimental

2.1. Synthesis and structural characterization of the catalysts

The ruthenium monometallic electrocatalysts were synthesized using 0.063 mmol of the precursor triruthenium dodecarbonyl [$\text{Ru}_3(\text{CO})_{12}$, Aldrich], mixed with 5 mL of 1,2-dichlorobenzene (b.p. 178–180 °C, Aldrich) and treated thermally using microwave irradiation at different power (80, 100 and 200 W) and time (30 and 60 min) conditions (Table 1) and at 180 °C. The product obtained was washed with isopropyl alcohol (J. T. Baker) and dried at room temperature. 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. For X-ray diffraction studies, a Rigaku D/max-2100, with $\text{Cu K}\alpha 1$ irradiation (1.5406 Å) was used. A Philips XL30ESEM microscope was used to obtain energy-dispersive X-ray spectra (EDS) of the catalysts.

2.2. Electrochemical experiments

2.2.1. Electrode preparation

The working electrode for the rotating disk electrode (RDE) study was prepared by mixing 1.7 mg of Vulcan[®] XC-72 (Cabot) and 0.3 mg of the catalyst with 10 μL of 5% Nafion[®] solution (ElectroChem) in an ultrasonic bath. 2 μL of the resulting mixture was deposited on a glassy carbon disk electrode and

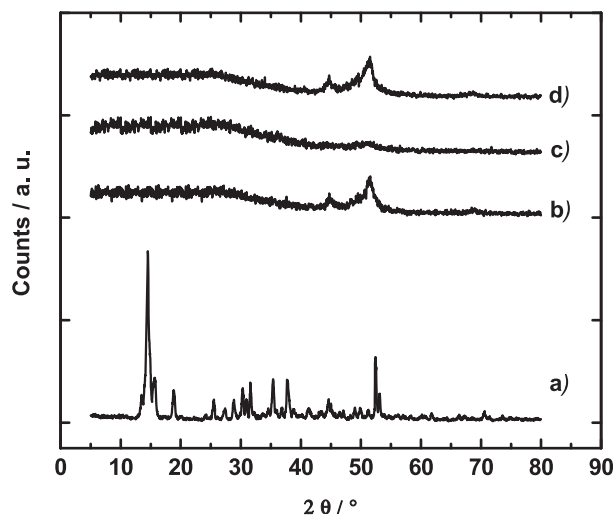


Fig. 2 – X-ray diffraction patterns for a) $\text{Ru}_3(\text{CO})_{12}$ and the ruthenium catalysts synthesized under the following conditions: b) 180 °C/30 min/80 W, c) 180 °C/30 min/100 W, d) 180 °C/60 min/100 W.

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