

Preparation and Characterization of RuO₂ Catalysts for Oxygen Evolution in a Solid Polymer Electrolyte

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RuO₂ electrocatalysts were synthesized and characterized for the oxygen evolution reaction in a Solid Polymer Electrolyte (SPE) electrolyzer. The catalysts were prepared by a colloidal preparation procedure and thermal treatment at different temperatures from 200 to 350 °C. The material characterization was carried out by XRD, TG-DSC and TEM analyses. The RuO₂ catalysts were sprayed onto a Nafion 115 membrane with a loading of 3 mg cm⁻². A Pt catalyst was used at the cathode compartment with a loading of 0.6 mg cm⁻². The electrochemical activity of MEAs was investigated in a single SPE cell and in a conventional three-electrode half-cell by using linear voltammetry, impedance spectroscopy and chronoamperometry. The maximum current density at high potential (1.8 V) was obtained for RuO₂ calcined at 300°C for 1 h. The chronoamperometric measurements shown that the most stable catalyst was the RuO₂ calcined at 300°C for 3 h.

Keywords: Water Electrolysis; RuO₂ catalyst; SPE electrolyzer

1. INTRODUCTION

Water electrolysis is traditionally carried out in alkaline media with several commercial electrolyzers available on the market. Water electrolyzers using a solid polymer electrolyte (SPE) are less common and generally utilize expensive materials such as noble metal electrocatalysts and sulphonated polymers with perfluorocarbon chains as proton exchange membranes (Nafion®)[1]. The

first electrolyzers using a polymer membrane as electrolyte were developed by General Electric Co. in 1996 for space applications [2].

The oxygen evolution reaction (OER) occurs at a suitable reaction rate on noble metal electrodes (e.g., Pt, Au, Ir, Rh, Ru, and Ag); however, metal oxides are generally more active electrocatalysts for this reaction than metal electrodes [3-5]. The most active oxides for the OER are RuO₂ and IrO₂ [6-14]. IrO₂ exhibits high corrosion-resistance properties, but slightly lower activity than RuO₂ [15]. From the point of view of electro-catalysis, it is important to consider the crystal-field stabilization energy, the dispersion, the crystallinity, and the crystallite size of these oxides. RuO_x is generally prepared by thermal decomposition of RuCl₃ [16], which is applied as thin coating on a metallic substrate, usually titanium. The properties of the oxide layer depend on several factors: technique of applying the salt solution, concentration of solution, temperature of calcination, time of heating, etc.

Various methods were developed for the synthesis of noble metals based oxides [17, 18], i.e. the Adams fusion method [19], sol-gel methods [20-24], polyol methods [9, 25]. The different methodologies can affect the properties of the obtained oxide materials.

Furthermore, various steps are necessary to complete the oxide powder synthesis. In the present study, a simple, fast and low cost method of preparation of a RuO₂ electro-catalyst, compared to the literature [26-28], was used.

A similar procedure was developed by Zheng et al. [29] for electrochemical capacitor applications; yet, in that case, the particle size was about 20 nm. This synthesis allowed us to obtain a crystalline phase with a suitable particle size (about 10 nm) at low temperatures with a yield of 95%. As reported by H. Ma et al. [28], particle sizes and heat treatment of the material influence the catalytic performance of RuO₂ for OER and the stability. Calcined RuO₂ with large particle sizes showed higher corrosion resistance than uncalcined and low-temperature treated materials [28]. For this reason, in the present study, the synthesized RuO₂ was subjected to different calcination temperatures and investigated in half-cell and single-cell experiments.

2. EXPERIMENTAL

2.1 Preparation of RuO₂ electrocatalysts

0.01 mol of RuCl₃•3H₂O (Aldrich) was dissolved in 100 mL of deionized water. The aqueous solution was then heated (100°C) under air atmosphere and magnetically stirred for 10 min. 1 ml of sodium hydroxide (1 M) was added to the solution in order to obtain the precursor Ru-hydroxide. The reaction mixture was maintained under stirring and heat (100°C) for 45 min. Afterwards, the solution was centrifuged for 10 minutes and filtered. The precipitate was washed several times with deionized water to remove the remaining chlorides. The Ru-hydroxide was dried for 5 h at 80°C. The dry paste was calcined in air at three different temperatures: 200, 300 and 350 °C for 1 h, using a heating ramp of 5 °C/min. Another sample was treated at 300°C for 3 h.

2.2 Physico-chemical characterization

XRD was performed on the dry electrocatalytic powders using a Philips X-Pert diffractometer that used as radiation source the $K\alpha$ line of the copper ($CuK\alpha$). The diffractometer was operated at 40 kV and 20 mA, a step time of 0.5 s $2\theta^{-1}$, and an angular resolution of 0.005° . The diffraction patterns were fitted to JCPDS (Joint Committee on Powder Diffraction Standards) and crystalline size distribution was calculated using LBA (line broadening analysis). The TG/DSC analysis was carried out in an STA 409C of NETZSCH - Gerätebau GmbH Thermal Analysis. The sample was heated from room temperature up to 550 °C at a heating rate of 5 °C/min under air atmosphere.

The morphology of catalysts was investigated by transmission electron microscopy (TEM) using a Philips CM12 instrument. Specimens were prepared by ultrasonic dispersion of the catalysts in isopropyl alcohol depositing a drop of suspension on a carbon-coated grid.

2.3 Preparation of working electrode for half-cell measurements

An aqueous solution (100 μ l) of catalyst (5 mg) was prepared and mixed in an ultrasonic bath. 2 μ l of aqueous solution of catalyst was deposited on a glassy carbon substrate; afterwards, the electrode was coated with 1 μ l of Nafion[®] solution (5% Aldrich). The behaviour of the various catalysts for oxygen evolution reaction was investigated by linear voltammetry (LV).

2.4 Half-cell electrochemical characterization

The electrochemical analyses were carried out at room temperature in a conventional three-electrode cell consisting of the ruthenium oxide electrode (working electrode), a reference electrode (Hg/HgSO₄ sat.) and a platinum grid (counter electrode). The electrolyte solution was 0.1 M H₂SO₄. An inert gas was fed to the solution for 30 min before the test. The cell was connected to an AUTOLAB PGSTAT 302 Metrohm potentiostat/galvanostat. To evaluate catalysts activity for OER, a linear voltammetry in a potential range from 1.20 V to 1.65 V vs. RHE was carried out.

2.5 Preparation of membrane and electrode assembly (MEA)

A Nafion 115 (Ion Power) membrane was used as solid polymer electrolyte. The oxygen evolution catalysts were directly deposited onto one side of the Nafion 115 by spray technique. Catalytic inks were composed of aqueous dispersions of catalyst, deionised water, Nafion[®] solution (5% Aldrich) and anhydrous Ethylic alcohol (Carlo Erba); the anode catalyst loading was about 3 mg cm^{-2} . A Ti/Pt (95:5) grid was used as backing layer. A commercial 30% Pt/Vulcan XC-72 (E-TEK, PEMEAS, Boston, USA) was used as catalyst for the H₂ evolution. The cathode electrode was prepared by directly mixing in an ultrasonic bath a suspension of Nafion ionomer in water with the catalyst powder. The obtained paste was spread on carbon cloth backings (GDL ELAT from E-TEK) with a Pt loading of 0.6 mg cm^{-2} . The ionomer content in both electrodes was 33 wt. % in the catalytic

layer after drying. MEAs were directly prepared in the cell housing by tightening at 9 N•m using a dynamometric wrench.

2.6 Electrochemical characterization of MEA

The SPE electrolyzer performance was evaluated in a temperature range from 25 to 80°C. Heated deionised water, which was circulated by a pump at a flow rate of 2 ml/min, was supplied to the anode compartment. The water temperature was maintained at the same cell temperature. Measurements of cell potential as a function of current density, electrochemical impedance spectroscopy (EIS) and chrono-amperometry were carried out by using an Autolab PGSTAT 302 Potentiostat/Galvanostat equipped with a 20 A booster (Metrohm).

3. RESULTS AND DISCUSSION

XRD analyses were carried out on the anode catalysts. Figure 1 shows XRD patterns of the precursor powder before and after calcination at 200, 300 and 350°C.

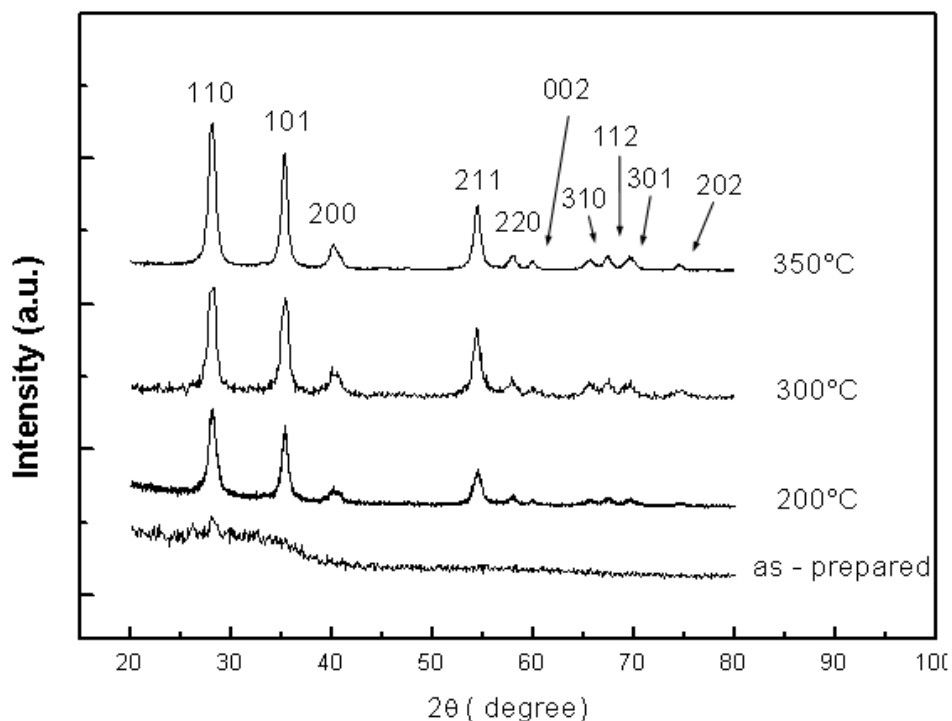


Figure 1. X-Ray diffraction patterns of RuO₂ as-prepared and calcined powders at various temperatures.

The XRD peaks were assigned to RuO₂ in a tetragonal crystallographic structure. No presence of Ru in a metallic form was found. The mean crystallite size was estimated from the broadening of

main peaks by the Debye-Scherrer equation. The crystallite size found was in an interval from 8 to 12 nm and it was similar for the powders calcined at the different temperatures. In order to investigate the precursor calcination process, a thermal analysis was carried out. The results of TGA and DSC measurements are shown in Figure 2.

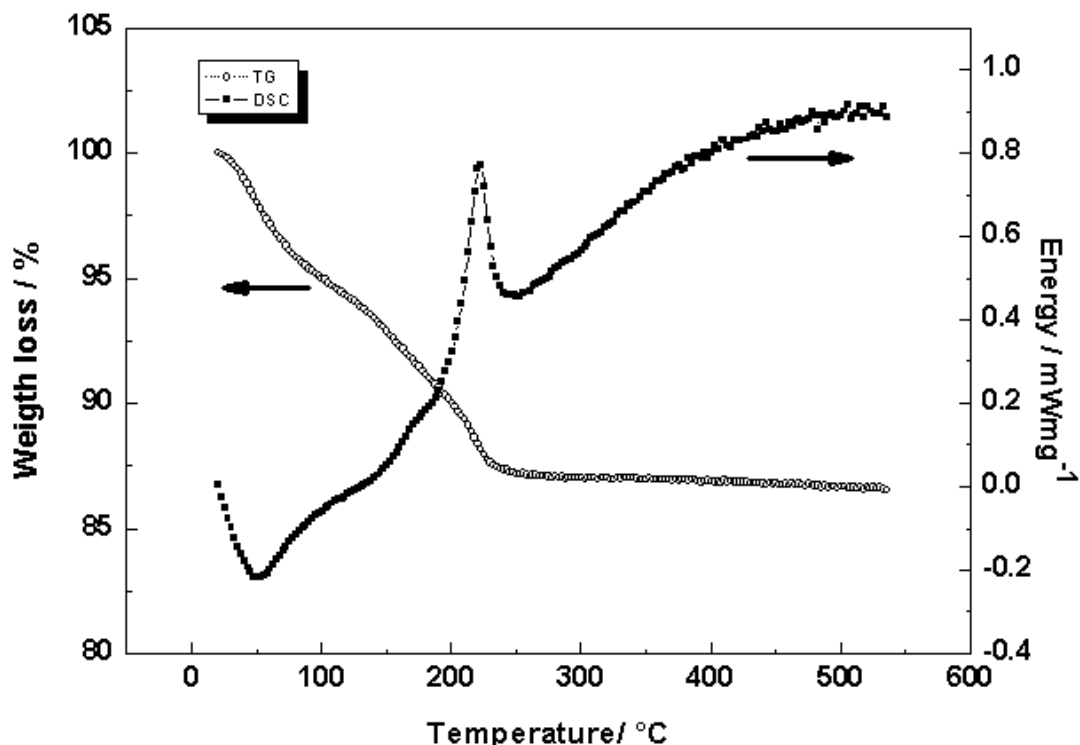


Figure 2. TGA and DSC curves of RuO_x as-prepared powder.

The first weight loss was assigned to physical dehydration (below 120°C); whereas, the second one was attributed to chemical dehydration (in the range $120\text{--}210^\circ\text{C}$). An endothermic peak was observed in the range $180\text{--}260^\circ\text{C}$ due to an amorphous to crystalline structure phase transition of RuO_2 as confirmed by XRD. Above 260°C a slight oxygen loss was recorded. Total weight losses of 14 wt.% were observed after treatment at 550°C .

Figure 3 shows the half-cell I-V curves for uncalcined and calcined samples. The best performance for the oxygen evolution reaction at ambient temperature was obtained for the RuO_2 powder calcinated at 300°C . The maximum current density was 180 mA cm^{-2} at 1.65 V. This catalyst was selected for the further investigations in an SPE electrolyzer. In order to evaluate the effect of duration of the thermal treatment, a RuO_2 calcined at 300°C for 3 h was also prepared for comparison.

In order to determine the morphology of the powders, TEM analysis was carried out on the amorphous precursor and on the most promising catalyst (sample calcinated at 300°C). Images are shown in Figures 4-5. From this analysis, agglomerates of small size appear to be present mainly in amorphous powder with a particle size of 1.8 nm; whereas, for the 300°C 1 h calcined powder, a crystalline structure with a particle size of about 9 nm was clearly observed. Processing of this TEM

image by Fourier transformations and using Carine crystallography software allowed to confirm the tetragonal crystal phase of RuO₂; a scheme representation of the crystal structure is presented in figure 6. The powder calcined for 3 h showed a similar morphology of the sample calcined for 1 h (not shown).

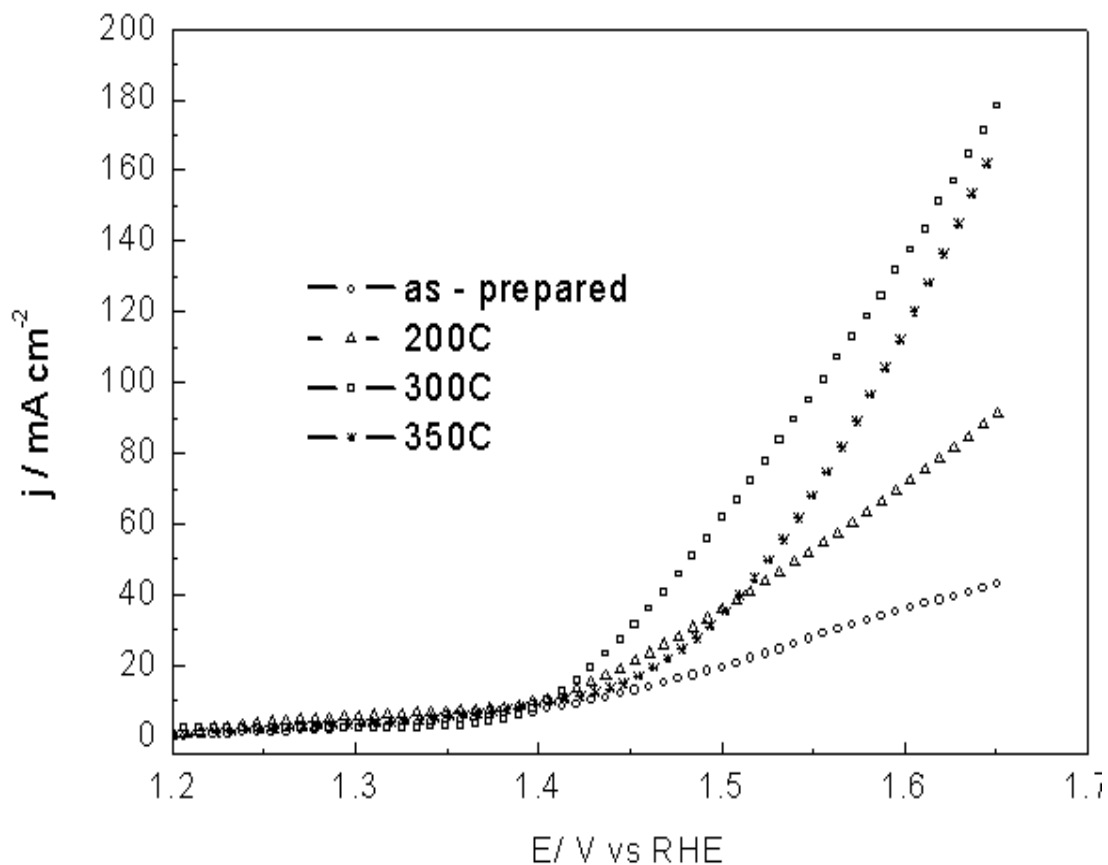
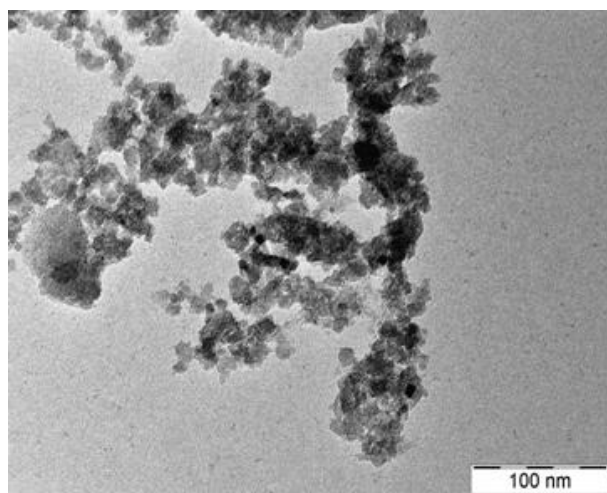
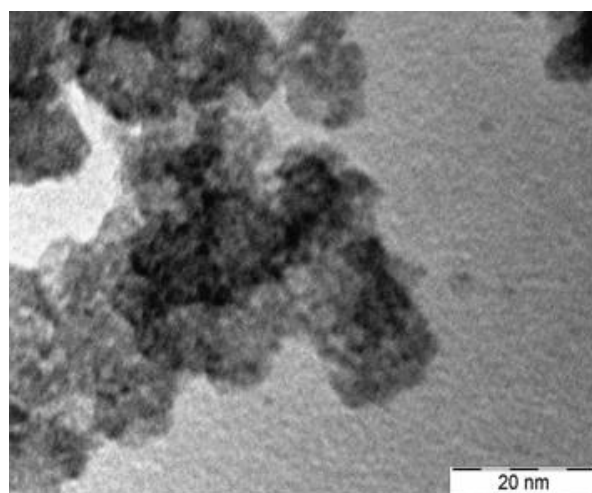


Figure 3. Linear Voltammetry of RuO₂ powder-based electrodes, synthesized and calcined at various temperatures, in 0.5 M H₂SO₄ half – cell at 25°C.



A



B

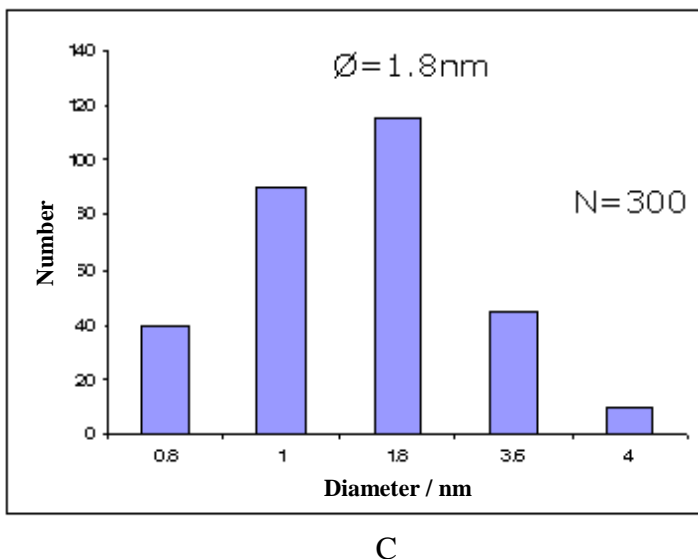
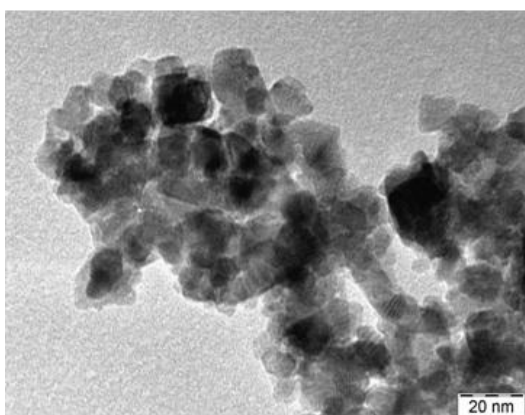
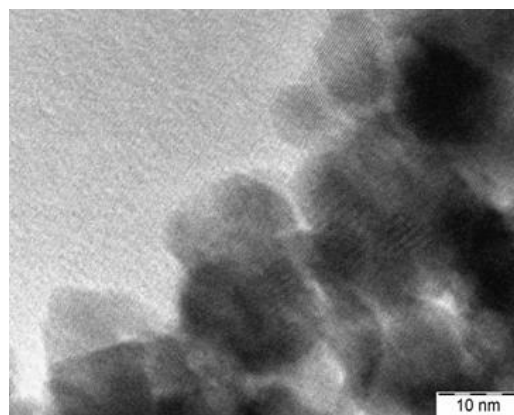


Figure 4. TEM micrographs of RuO_x synthesized: (A) and (B) at different magnifications (C) Particle size distribution analysis.



A



B

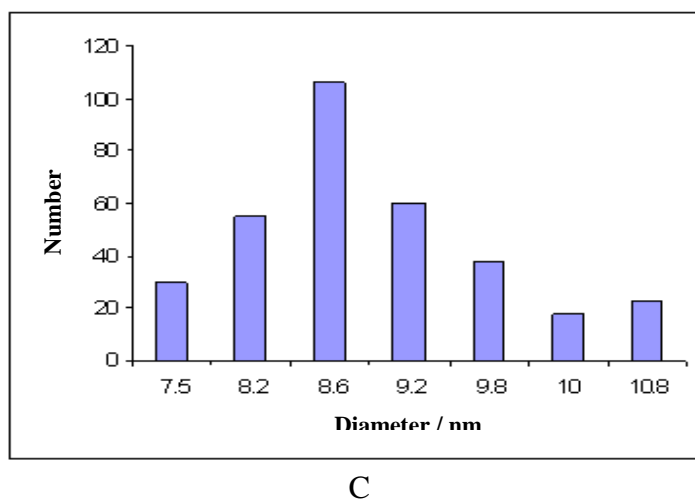


Figure 5. TEM micrographs of RuO₂ calcined at 300 °C/1 h: (A) and (B) at different magnifications (C) Particle size distribution analysis.

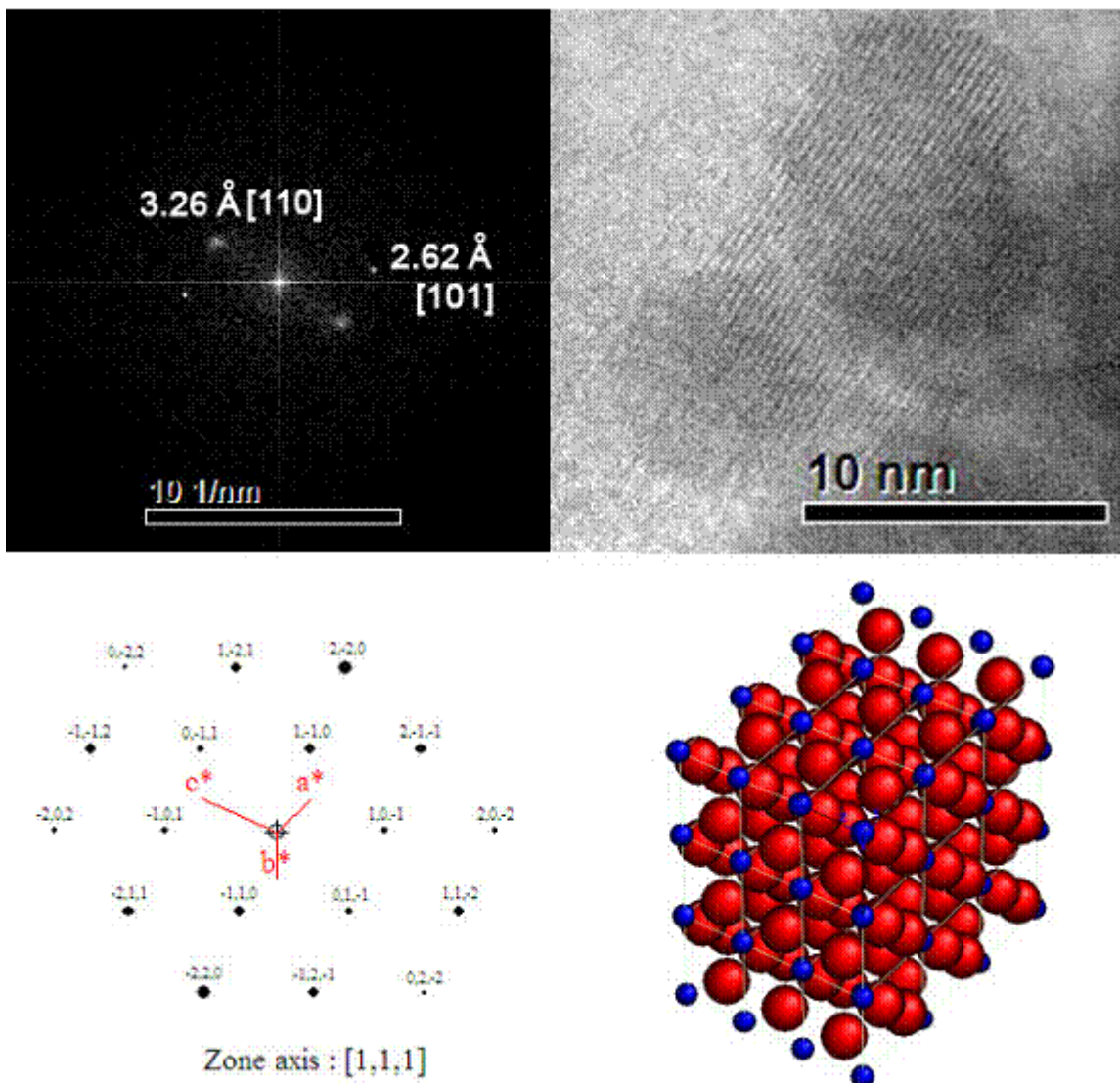


Figure 6. TEM image of RuO₂ calcined at 300 °C/1 h: Scheme representation of tetragonal RuO₂ crystal structure by Carine Crystallography Software

The three samples were analyzed in a SPE single cell electrolyzer. Series and charge transfer resistances were evaluated by means of EIS at 1.5 V. Figure 7 shows the EIS spectra of electrolyzers with the above mentioned catalysts at 80°C under atmospheric pressure. The impedance plots (Nyquist) reveal a larger series and charge transfer resistance for the amorphous RuO₂ than the calcined ones. The minimum in the series resistance was observed for the electrolyzer with the powder calcined at 300°C for 1h with a value of 0.19 ohm•cm²; whereas, the lowest charge transfer resistance was obtained for the sample calcined for 3 h, i.e. 0.085 ohm•cm².

Figure 8 shows the I-V curves at 80°C under atmospheric pressure for the amorphous sample and for the powder after calcination at 300 °C for 1 h and 3 h. The electrocatalyst performance in the single cell is significantly larger than in half cell primarily due to the higher noble metal loading in the

MEA electrodes. A contribution of sulfate anions adsorption in determining a poorer performance on half cell experiments is not discarded.

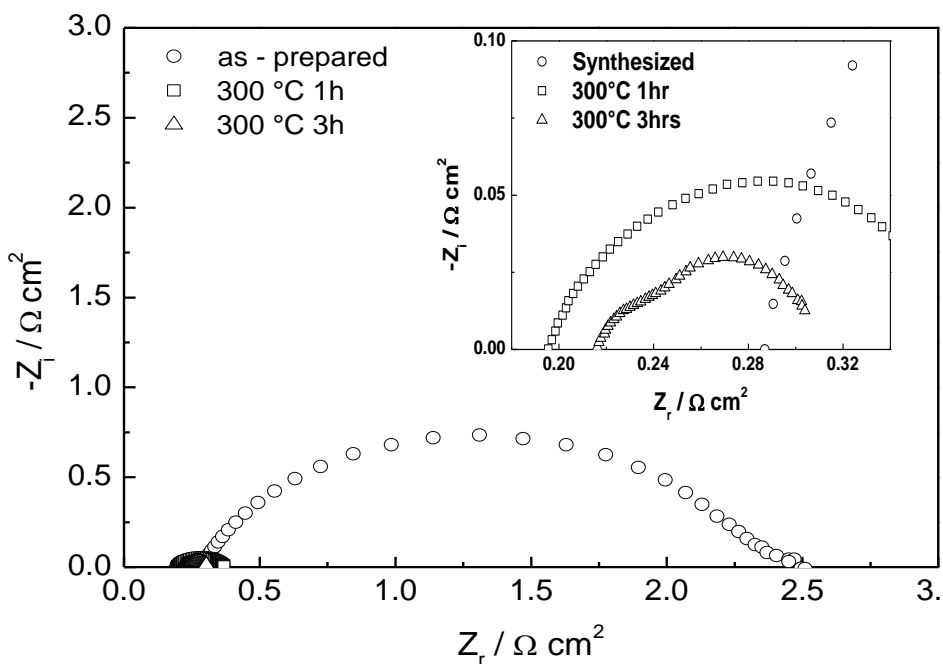


Figure 7. Impedance Spectroscopy of the SPE electrolyzer based on RuO₂ electrocatalysts, as-prepared and calcined at 300°C for 1 h and 3 h at 80°C and 1.5 V.

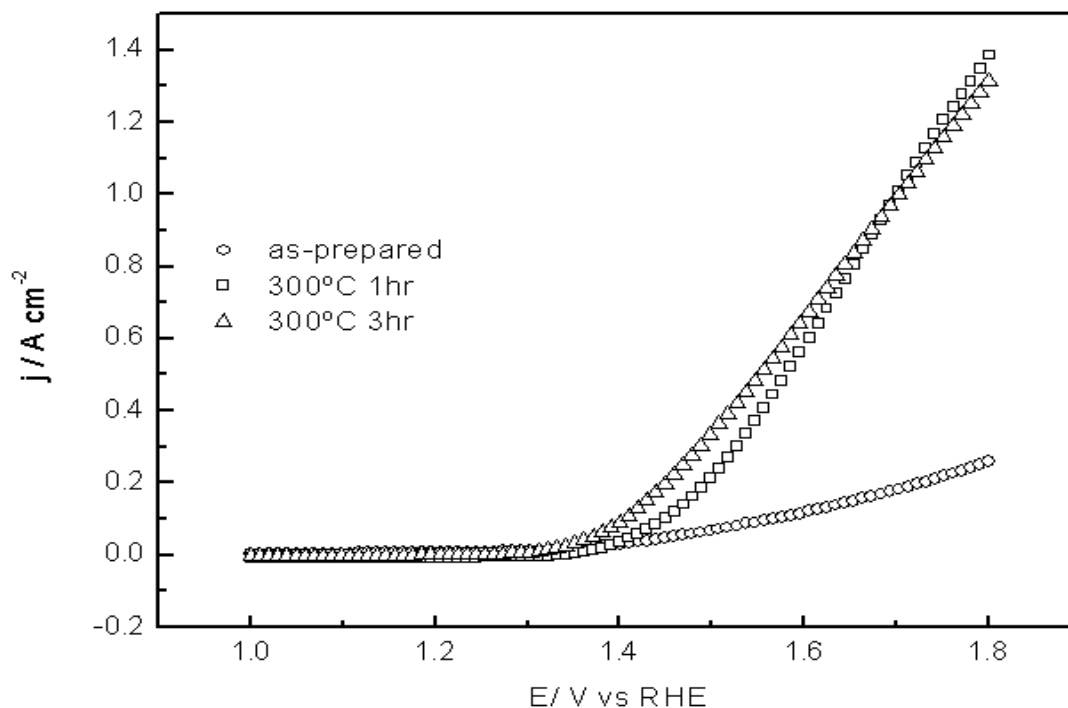


Figure 8. Linear Voltammetry of the SPE electrolyzer based on RuO₂ powders, as-prepared and calcined at 300°C for 1 h and 3 h at 80°C.

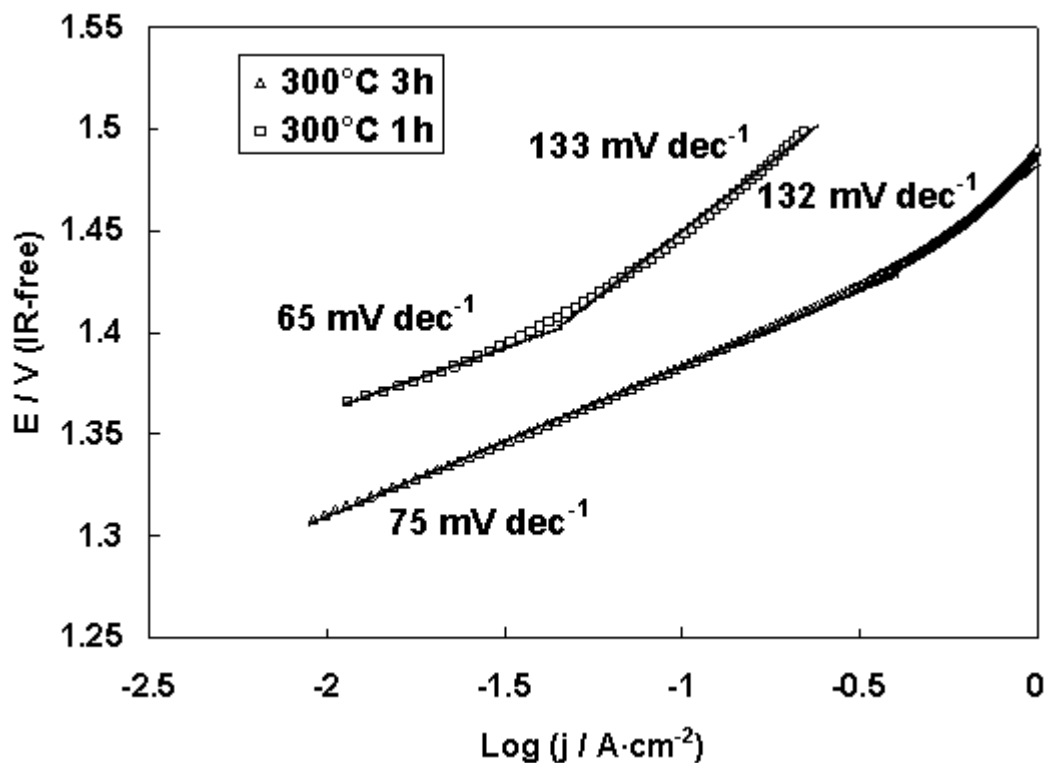


Figure 9. Tafel plot for oxygen evolution reaction in a SPE electrolyser for the RuO₂ powder calcined at 300°C for 1 h and 3 h at 80°C.

The cell equipped with RuO₂ calcined at 300°C for 3 h showed an onset for the OER more shifted towards lower potentials according to the lower charge transfer resistance obtained by the EIS analysis. This indicates a better catalytic activity of this catalyst probably due to a suitable crystalline structure. The cell based on RuO₂ calcined at 300°C for 1 h showed a higher onset potential for OER than the previous one, but a better behavior in terms of ohmic characteristics, according to a lower series resistance recorded by EIS analysis for this cell. Thus, the maximum current density at high potential (1.8 V) was obtained using RuO₂ calcined at 300°C for 1 h; it was about 1.4 A cm⁻².

This performance appears to be comparable to the state of art [30-34] in this field and it appears promising if one considers that a simple catalyst preparation method, which can be subjected to further improvement, was used.

The ohmic-drop-corrected Tafel plots for oxygen evolution reaction at the RuO₂ electrocatalysts calcined at 300°C for 1 h and 3 h are shown in Figure 9. Two Tafel slopes have been identified for the oxygen evolution process at 80°C in the PEM electrolyser. At low current densities, the Tafel slope is 65-75 mV•dec⁻¹, whereas at large current densities it is 132-133 mV•dec⁻¹. These values are similar to those already observed in the literature at room temperature for the oxygen evolution process with oxide based electrodes [15, 35-38]; i. e., 60 mV•dec⁻¹ and 120 mV•dec⁻¹ in the low and high current density range respectively.

A Tafel slope of 120 mV•dec⁻¹ is generally attributed to the dissociative water adsorption with release of a proton and electron according to the following mechanism:



The low Tafel slope can be attributed to the presence of adsorption intermediates involving OH species on the electrode surface with different energy states [15, 35]. It is not discarded a possible contribution to the rate determining step of the electrochemical desorption of a proton from the adsorbed OH species as reaction intermediates at low current densities.

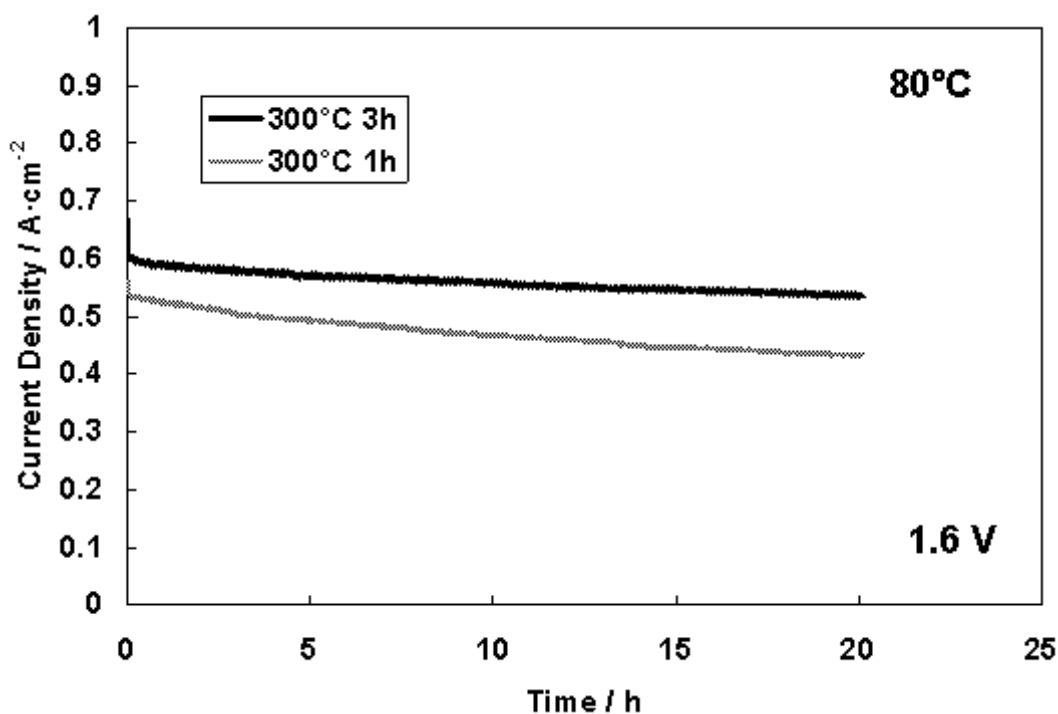


Figure 10. Chronoamperometric measurement of the SPE electrolyser based on RuO_2 calcined at 300°C for 1 h and 3 h at 80°C

Figure 10 shows the chronoamperometric measurements carried out at 80°C and atmospheric pressure for the RuO_2 electrocatalysts calcined at 300°C for 1 h and 3 h. These experiments were performed at a potential of 1.6 V for 20 hours. The cell equipped with RuO_2 calcined at 300°C for 3 h showed a higher current density compared to the cell equipped with RuO_2 calcined at 300°C for 1 h. This evidence was in agreement with the I-E curves (Fig. 8). It was observed that the current density slightly decreased during the time for both measurements. This could be due to the presence of small particles in the catalysts that can be more subjected to corrosion; on the contrary of large RuO_2 particles which appear to be sufficiently stable [28]. However, our evidences confirm the low stability of RuO_2 that was discussed in several papers in the literature [12, 13]. The largest loss was showed with RuO_2 calcined at 300°C for 1 h. This could be due to the higher stability of RuO_2 particles calcined for 3 h compared to RuO_2 particles calcined for 1 h. However, an increase of the RuO_2 particle size causes a decrease of catalytic activity for oxygen evolution for the sample calcined at 350°C . Further studies are in due course to assess the stability of larger RuO_2 nanoparticles. Another

strategy to improve the stability of the RuO₂ electrocatalyst relies on the use of IrO₂-RuO₂ solid solutions. The aim is to reach a good compromise between stability and performance.

4. CONCLUSIONS

A simple, fast and low temperature colloidal method for the obtainment of RuO₂ nano-particles was developed. Catalysts were prepared by colloidal deposition at a temperature near to 100°C and, successively, calcined at different temperatures from 200 to 350°C. The physico-chemical characterization was carried out by XRD, TG-DSC and TEM analyses. The electrochemical activity of these catalysts as anodes in an SPE electrolyzer was investigated. The maximum current density at high potential (1.8 V) was obtained using RuO₂ calcined at 300°C for 1 h; it was about 1.4 A cm⁻². Yet, the best results were obtained for the RuO₂ calcined at 300°C for 3 h in the chronoamperometric measurements with a higher current density at 1.6 V for 20 hours compared to the RuO₂ calcined at 300°C for 1 h. However, chronoamperometric measurements showed a slightly decrease of performances with time. A further optimization of the physico-chemical proprieties of these materials is necessary in order to increase the stability and performance for application in a PEM electrolyzer.

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