JOURNAL OF APPLIED ELECTROCHEMISTRY **27** (1997) 1323–1327

Ruthenium dioxide films on titanium wire electrodes by spray pyrolysis: preparation and electrochemical characterization

J. L. FERNÁNDEZ, M. R. GENNERO DE CHIALVO, A. C. CHIALVO

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, 3000 Santa Fe, Argentina

Received 21 September 1996; revised 20 March 1997

A device for the preparation of thick and uniform films of ruthenium dioxide on titanium wires by the spray pyrolysis technique has been developed. The details of the apparatus, as well as the operation conditions, are described. The electrodes obtained were characterized by X-ray diffraction analysis, scanning electron microscopy and cyclic voltammetry. Their electrocatalytic activity for chlorine evolution were also evaluated, as well as their stability through an accelerated test of service life.

Keywords: *ruthenium dioxide films*, *spray pyrolysis*, *chlorine evolution*

1. Introduction

The preparation of electrodes covered with films of pure or mixed oxides is usually carried out by thermal decomposition of thin layers of a precursor previously deposited on the substrate surface. This precursor is obtained by partial or total evaporation of solutions containing the cation of the oxide to be prepared or the corresponding cations in appropriate ratio if the final product is a mixed oxide. The precursor layers are deposited on the substrate by different techniques such as painting, brushing, dipping etc. [1]. The resulting layer is dried at a moderate temperature. This procedure is repeated several times until the desired coating thickness is achieved. Subsequent thermal treatment at temperatures between 300 and 600 °C is needed to decompose the precursor in the corresponding oxide.

An alternative method, spray pyrolysis, consists in the generation of droplets of the precursor solution through an atomizer. These small drops are sprayed on the surface to be covered. This surface must be maintained at an adequate and constant temperature to produce vaporization of the solvent and subsequent decomposition of the precursor. This technique, originally proposed by Chamberlin [2], was applied for the preparation of films of Fe_2O_3 [3], CdO [4], Co_3O_4 [5], $NiCo_2O_4$ [5], SnO_2–Sb_2O_5 [6], SnO_2 [7] and $Cu_{1.4}Mn_{1.6}O_4$ [8]. Nevertheless, this procedure was designed for application to plane surfaces and therefore it cannot be used for the preparation of oxide coatings on cylindrical electrodes.

The aim of the present work is to develop an alternative technique for the preparation of oxide coatings on cylindrical electrodes by the spray pyrolysis technique. The proposed method was applied to the preparation of ruthenium dioxide films on titanium wires, which were characterized later by different techniques. Their electrocatalytic behaviour for chlorine evolution was also evaluated as well as their stability through an accelerated test of service life. Furthermore, several experiments were carried out in order to obtain other types of oxide layer of interest in electrocatalysis, using different precursor solutions and substrates.

2. Experimental details

2.1. *Spray pyrolysis device*

Figure 1 shows a simplified scheme of the apparatus developed for the application of the spray pyrolysis technique. The oxide film is obtained by the impact of a flow of small droplets of the precursor solution on a rotating wire of the metal substrate, which is heated by the flow of an electric current. The droplets are produced in a small chamber by a piezoelectric vibratory atomizer (100 MHz), located at the bottom of the chamber and transported by air flow. In the conditions used, the rate of consumption of the precursor solution is $0.35\,cm^3\,min^{-1}$. The resulting drops have good uniformity, with a diameter ranging between 1.5 and 2 μm. The droplet size was determined by sedimentation of the droplets onto a glass slide covered with a film of light oil and then measurement with an optical microscope.

The droplets are directed towards the titanium wire by a nozzle, emerging from it at a speed of $40\,cm\,s^{-1}$. The uniformity of the oxide film is achieved by the continuous rotation of the substrate, at a rotation rate of 4 rpm.

0021-891X

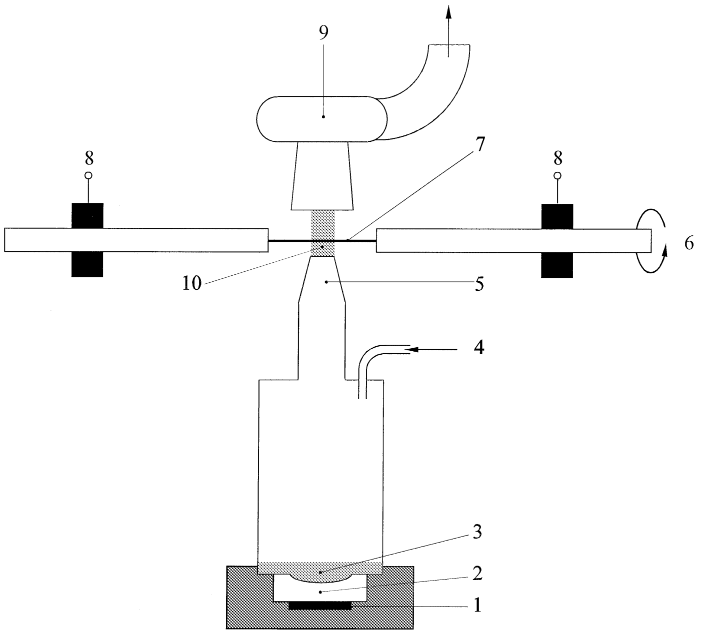

Fig. 1. Scheme of spray pyrolysis device. Key: (1) piezoelectric crystal, (2) water, (3) precursor solution, (4) air inlet, (5) nozzle, (6) wire support rotating axis, (7) titanium wire, (8) electrical connections, (9) extraction system and (10) aerosol flow.

2.2. *Electrode preparation and characterization*

The precursor solution used was prepared by dissolving $RuCl_3$ in an aqueous solution of 6 M HCl. The concentration of Ru(III) was varied in the range 0.01 to 0.1 M, being determined by u.v.–visible spectrophotometric analysis [9]. The experiments described in the present work correspond to a concentration of 0.024 M $RuCl_3$, except where otherwise stated. Precursor solutions were prepared using analytical grade reagents and triply distilled water.

The substrate was a 99.7% pure titanium wire of 0.8 mm diameter, which was subjected to pretreatment consisting of mechanical polishing with emery paper and chemical etching in hot 10% oxalic acid solution for one hour. It was then rinsed with triply distilled water, placed in the spray pyrolysis device and heated by Joule effect at $2\,W\,cm^{-1}$. The time of application of the spray pyrolysis technique was varied between 5 and 30 min.

The characterization of the ruthenium dioxide film was carried out by optical microscopy (Nikon Optiphot), scanning electron microscopy (Jeol JSM-35C) and X-ray diffraction (Shimadzu XD-D1), using CuK_α radiation. Electrochemical characterization was also carried out by cyclic voltammetry.

2.3. *Electrochemical studies*

Electrochemical measurements were carried out in a conventional three-electrode, three compartment, Pyrex glass cell. The counterelectrode was a platinum wire of $10\,cm^2$ geometric area. Applied potentials were measured against a saturated calomel electrode. Special attention was paid to the construction and location of the Luggin–Haber tip so as to ensure negligible ohmic drops. The working electrodes were ruthenium dioxide coatings on titanium wires obtained by the method described above. Electrolyte solutions were made up using analytical grade reagents and triply distilled water. All measurements were carried out at 30 ± 0.1 °C.

The solution used for the study of the electrocatalytic activity of the ruthenium dioxide electrodes for chlorine evolution (ClER) was 3.0 M NaCl, with pH adjusted to 2.0 with HCl. The ClER evaluation consisted mainly in the application of slow potentiodynamic sweeps ($10^{-4}\,V\,s^{-1}$). The values of the current density were calculated on the basis of the geometric electrode area. Cyclic voltammetry was carried out in the same solution at a sweep rate of $0.1\,V\,s^{-1}$.

The accelerated service life tests were done by the method proposed by Loucka [10], in a 0.5 M H_2SO_4 solution, applying a current density of $1\,A\,cm^{-2}$ to the ruthenium dioxide electrode.

3. Results

3.1. *Characterization of the dioxide film*

A layer with excellent covering properties was formed as illustrated in the micrographs of Fig. 2. These correspond to an electrode prepared with a 0.024 M $RuCl_3$ solution and a time of application of 30 min. The resulting oxide film is dark grey coloured, with a slight blue tinge. Figure 2(a) and (b) shows the morphology of this electrode at two different magnifications, respectively. A more compact and less porous oxide layer was obtainable using higher concentrations of the precursor solution.

Oxide samples obtained by peeling off the covering layer were analysed by X-ray diffraction. Figure 3 shows the resulting diffraction pattern, where three

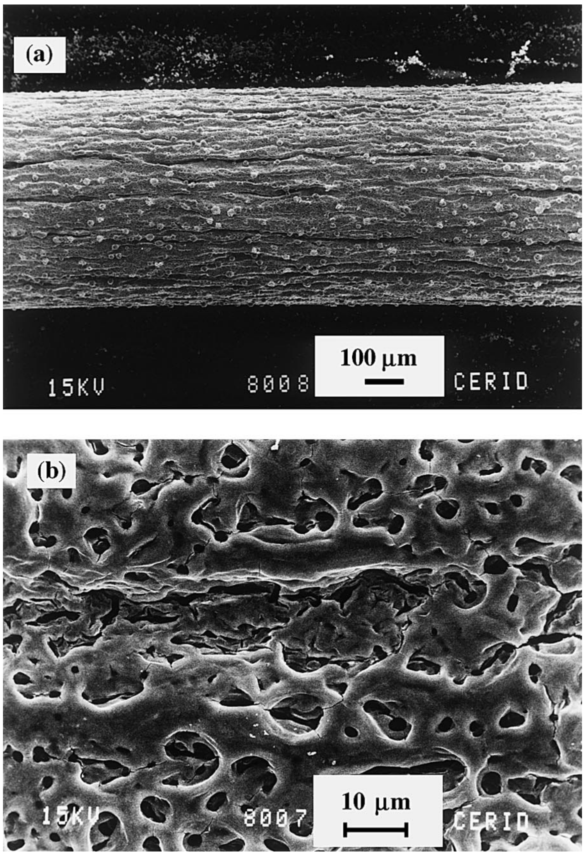

Fig. 2. SEM micrographs of a ruthenium dioxide coating. Precursor solution 0.024 M $RuCl_3$; time of spraying 30 min. Scale bars: (a) 100 μm; (b) 10 μm.

well defined peaks located at $2\theta = 28.0°$, 34.9° and 54.0° are seen. These correspond to the crystallographic planes (1 1 0), (1 0 1) and (2 1 1), respectively, which characterizes the rutile structure of the film [11–14].

The potentiodynamic response of the electrodes was evaluated in a 3.0 M NaCl solution, pH 2.0, by the application of cyclic voltammetry at a sweep of 0.1 V s^{-1} at 30 °C. Figure 4 shows the resulting voltammogram, which is coincident with that found in the literature [12] for similar conditions.

3.2. *Electrocatalytic activity for chlorine evolution*

The electrocatalytic activity of oxide coated titanium wires obtained under different operation conditions of the oxide growth process was evaluated for chlorine evolution. Experiments were carried out in 3.0 M NaCl solution, pH 2.0. The working electrode was held potentiostatically at 1.2 V during 30 min to saturate the solution with chlorine gas and then a slow potentiodynamic sweep (10^{-4} V s^{-1}) was applied between 1.2 and 1.0 V. The variation of the logarithm of the experimental current density on the applied potential (log *i*/*E*) shows the existence of one or two pseudo Tafelian domains with Tafel slopes ranging between 20 to 40 mV dec^{-1}, depending on the conditions of the oxide layer formation. Figure 5 illustrates the case corresponding to a concentration of the precursor solution of 0.024 M $RuCl_3$ and a time of spraying equal to 30 min. Two Tafel regions can be distinguished, with slopes of 39 mV dec^{-1} for the low overpotentials and 26 mV dec^{-1} for the high overpotentials, respectively.

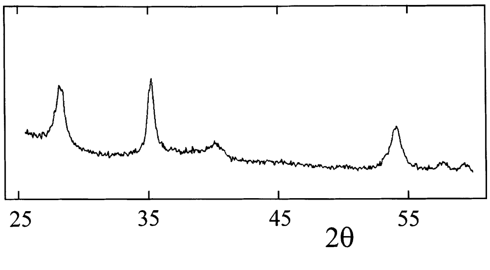

Fig. 3. X ray diffraction pattern of ruthenium dioxide powder. Precursor solution: 0.024 M $RuCl_3$.

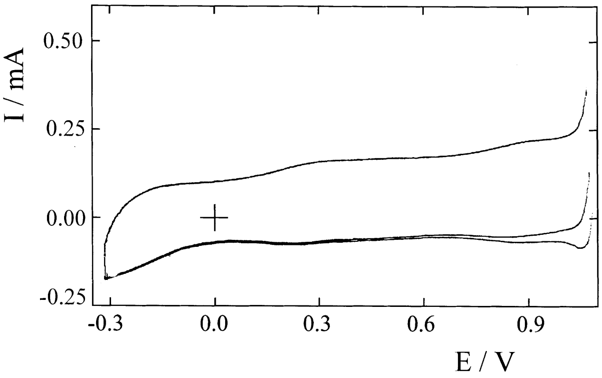

Fig. 4. Potentiodynamic profile of ruthenium dioxide electrode. NaCl 3 M, pH 2. Sweep rate 0.1 V s^{-1}. Preparation conditions: same as Fig. 2.

3.3. *Stability of the dioxide film*

The stability of the ruthenium dioxide coatings was evaluated by the accelerated test proposed by Loucka

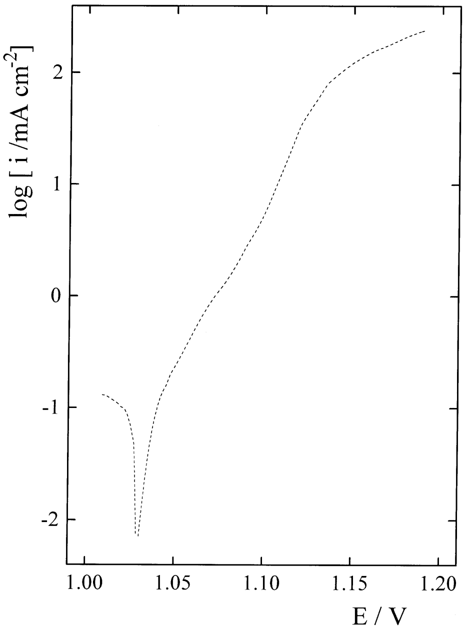

Fig. 5. Tafel dependence of ruthenium dioxide electrode. NaCl 3 M, pH 2. Preparation conditions: same as Fig. 2.

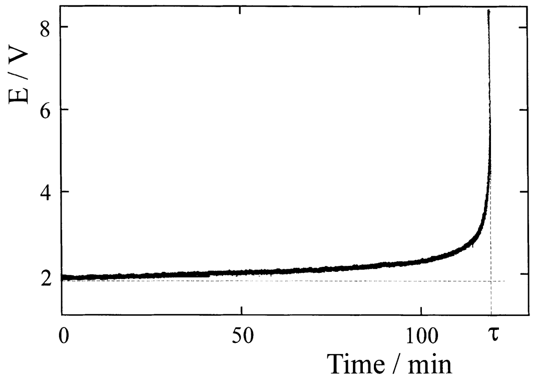

Fig. 6. Potential against time dependence of ruthenium dioxide electrode on the accelerated life test. 0.5 M H_2SO_4. Current density 1 A cm^{-2}. Precursor solution 0.079 M $RuCl_3$; spraying time 4 min.

[10]. It consisted in the application of a galvanostatic pulse in a 0.5 M H_2SO_4 solution and the evaluation of the dependence of the electrode potential with time. A typical potential vs. time response is illustrated in Fig. 6, corresponding to an electrode obtained from a precursor solution with a concentration of 0.079 M $RuCl_3$ and a time of spraying of 4 min. The time corresponding to the loss of the electroactive material is clearly determined by the sudden increase in the electrode potential and it is often called time-to-failure (τ) [15]. A similar behaviour was obtained in all the electrodes analysed.

The influence of the time of oxide growth, defined as the time of application of spray pyrolysis, on stability of the oxide film was studied as well as that of the concentration of the precursor solution. Figure 7 shows the dependence of the time-to-failure on the time of spraying at two different concentrations of precursor solution, 0.014 and 0.079 M $RuCl_3$, respectively. It can be noticed a marked influence of the composition of precursor solution, obtaining at the higher concentration very stable films at short times of spraying. These results can be favourably compared with those found by Loucka for titanium electrodes covered by a RuO_2 film generated from ethanol solutions of $RuCl_3$ [10].

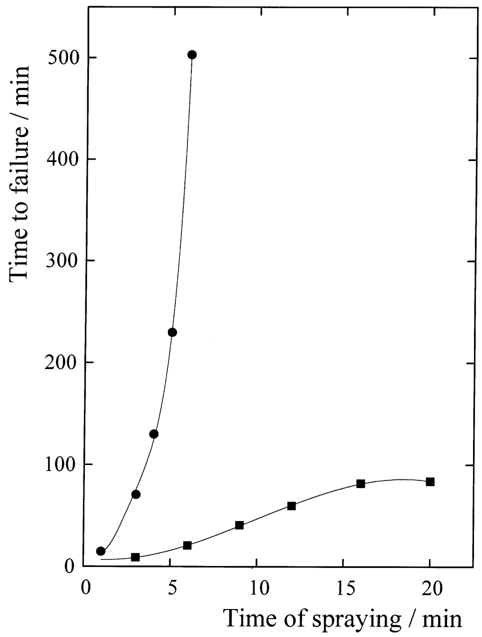

Fig. 7. Time-to-failure against time of spraying relationship of ruthenium dioxide electrode obtained by the accelerated life test. Precursor solution: (●) 0.079 M $RuCl_3$; (■) 0.014 M $RuCl_3$.

4. Discussion

Covering of conducting or insulating substrates by adhesive oxides can be done by spray pyrolysis technique using adequate precursor solutions and appropriate decomposition temperatures. Nevertheless, the usual devices in this method are not directly applicable for covering wires. In this case, as the substrate area is much less than that of a plate, the amount of precursor solution needed is at least an order of magnitude less than in the usual systems of spraying flat surfaces through nozzles. Furthermore, the relative displacement of substrate with respect to nozzle should be different to ensure uniformity of the surface covering. The first aspect has been solved substituting the conventional nozzles by a fog chamber. The haze of the precursor solution is obtained by the action of a piezoelectric crystal, which transmits to the solution a vibrational movement of high frequency, generating droplets with high uniformity in size, which are conducted towards the substrate by a controlled air flow.

The second aspect, related to a homogeneous distribution of the oxide layer on the wire surface, has been reached by rotation of the substrate, which is heated by the passage of an electric current. It should be noticed that on its trajectory towards the substrate wire, the droplet passes through a profile of raising temperature due to the dissipation of heat originated in the Joule effect to the surroundings. The aerosol drop undergoes a solvent evaporation process during this displacement, being possible also the occurrence of an incipient decomposition of precursor. On steady state, the endothermic dehydration process and the exothermic precursor decomposition [16] define the profile of temperature around the wire. This profile, and consequently the characteristics of the oxide layer, depends on operation conditions (electric power, flow rate, concentration etc.). All these variables were optimized in order to produce a ruthenium oxide film with a rutile structure, as it was confirmed by the X-ray diffraction pattern as well as the potentiodynamic response. Furthermore, scanning electron micrographs show that the oxide layer can have a compact or reticulated structure, depending on preparation conditions. The last one implies a high value of the roughness factor, a characteristic largely appreciated in the development of electrocatalysts. This fact can justify the low values obtained for Tafel slopes, suggesting the Cl_2 removal as the rate-determining step [17].

Another aspect to be taken into account is that during the growth process the whole film does not necessarily reach a crystalline structure, so the application of a subsequent thermal treatment should be useful. This can be done by passing an electric current through the wire electrode or by annealing it in a furnace at appropriate temperatures and times.

Finally, it should be mentioned that Co_3O_4 films on nickel and stainless steel wires were also obtained by this technique. The oxide layers have shown in this case the spinel structure with characteristics and properties similar to those obtained by other techniques [18, 19].

It can be concluded that the modification of the spray pyrolysis technique described in the present work allows to prepare cylindrical electrodes covered with an oxide layer in a rather simple and fast manner.

Acknowledgement

This work was supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). J.L.F. gratefully acknowledges the Universidad Nacional del Litoral for the research scholarship.

References

[1] S. Trasatti and G. Lodi, *in* 'Electrodes of conductive metallic oxides' (edited by S. Trasatti), Part A, Elsevier, Amsterdam (1980), chapter 7.
[2] R.R. Chamberlin and J. J. Skarman, *J. Electrochem. Soc.* **113** (1966) 86.
[3] J. C. Viguié and J. Spitz, *ibid.* **122** (1975) 585.
[4] J. F. Koenig, A. Sehili, M. Hamdani and P. Chartier, *J. Appl. Electrochem.* **14** (1984) 241.
[5] M. Hamdani, J. F. Koenig and P. Chartier, *ibid.* **18** (1988) 561.
[6] B. Correa-Lozano, C. H. Comninellis and A. De Battisti, *ibid.* **26** (1996) 83.
[7] J. Brunaux, H. Cachet, M. Froment and A. Messad, *Electrochim. Acta* **39** (1994) 1251.
[8] A. Restovic, G. Poillerat, J. F. Koenig, P. Chartier and J. L. Gautier, *Thin Solid Films* **199** (1991) 139.
[9] G. H. Ayres and F. Young, *Anal. Chem.* **22** (1950) 1277.
[10] T. Loucka, *J. Appl. Electrochem.* **7** (1977) 211.
[11] C. Iwakura, K. Irao and H. Tamura, *Electrochim. Acta* **22** (1977) 335.
[12] M. D. Spasojevic, N. V. Krstajic and M. M. Jaksic, *J. Res. Inst. Catalisis Hokkaido Univ.* **31** (1983) 213.
[13] F. Hine, M. Yasuda and T. Yoshida, *J. Electrochem. Soc.* **124** (1977) 500.
[14] ASTM X-ray Powder Diffraction Files, 21-1172 and 40-1290.
[15] F. Hine, M. Yasuda, T. Noda, T. Yoshida and J. Okuda, *J. Electrochem. Soc.* **126** (1979) 1439.
[16] G. Jang and K. Rajeshwar, *J. Electrochem. Soc.* **134** (1987) 1830.
[17] V. V. Losev, *Elektrokhimiya* **17** (1981) 733.
[18] M. R. Gennero de Chialvo and A. C. Chialvo, *Electrochim. Acta* **38** (1993) 2247.
[19] *Idem*, *ibid.* **35** (1990) 437.