



Single cell study of electrodeposited cathodic electrodes based on Pt–WO₃ for polymer electrolyte fuel cells

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ABSTRACT

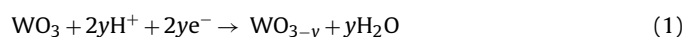
Cathodic electrodes based on electrodeposited Pt–WO₃ material for proton exchange membrane fuel cells (PEMFC) were studied in single cell configuration. Preparation of the electrodes was carried out by electrodeposition of Pt and WO₃ on commercial gas diffusion layer substrates (microporous carbon black layer on carbon cloth, ELAT E-TEK). The process of simultaneous electrodeposition of Pt and WO₃ is first analyzed from voltammetric curves. It is observed that the deposition of Pt is enhanced when WO₃ is present. Compositional analysis of the electrodes shows metallic platinum and WO₃ in variable proportions. The electrodeposited electrodes were characterized in single PEMFC. Membrane–electrode assemblies were prepared with Nafion[®] 117 electrolyte membrane and a standard Pt/C anode. Pt–WO₃ electrodes showed enhanced stability and good response in single cell up to 1500 h. Performance degradation is attributed to a decrease in Pt electroactive area and increase of the internal resistance of the cell. These effects are possibly a consequence of the production of mobile tungsten species, like soluble WO₂ at high current demands and low cathode potentials.

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1. Introduction

Tungsten-containing materials have been tested for the use in various types of fuel cells, as polymer electrolyte membrane fuel cells fuelled with hydrogen (PEMFCs), methanol (DMFCs) or ethanol (DEFCs), microbial fuel cells (MFCs) and molten carbonate fuel cells (MCFCs) [1]. They possess a wide variety of properties that allow them to play different roles in fuel cells, as catalysts, catalyst supports, co-catalysts, or proton conducting materials in membranes. Among them, tungsten bronzes, M_xWO₃, show good electronic and protonic conductivities, partially due to their non-stoichiometric composition [2]. They are non soluble in water and acids and can be easily deposited forming highly porous films, which permits the development of catalysts with high specific surface area. Moreover, they present catalytic properties for the reduction of hydrogen peroxide and the oxidation of hydrogen and methanol [3,4].

Non-stoichiometric oxides and tungsten bronzes are formed by means of electrochemical reactions from WO₃ in acidic mediums at voltages below 0.4 V versus NHE [5], Eqs. (1) and (2), respectively:



Nowadays, materials based on Pt and tungsten bronzes undergo an extensive research effort as co-catalysts, due to enhanced tolerance to CO, a key feature for both PEMFC and DMFC [6–10]. The properties that make them interesting for the use in the cathode of a PEMFC are, mainly, their high protonic conductivity and catalytic activity for decomposing hydrogen peroxide, which is an intermediate compound produced during the electroreduction of oxygen in the cathode, corrosive to carbon and the membrane. Even though a number of communications about basic aspects of the catalytic activity of Pt–WO₃ can be found in the literature [1], a significant lower number of reported works are devoted to testing these materials in a PEM single cell/stack, see references [11–13] for recent examples.

The electrodeposition method is a suitable and well documented option for the preparation of catalysts based on Pt–WO₃ [3,4]. It presents several advantageous properties to be applied to the preparation of catalyst layers: the synthesis and deposition of the catalyst occur simultaneously, resulting a strong interaction between the active phase and the support. This may lead to enhanced electrode stability. In addition, it usually takes place at moderate or low temperature, and, under certain conditions, the composition and morphology of the deposits may be controlled. A usual route to deposit Pt is based on hexachloroplatinic acid solutions, yielding normally high faradaic efficiencies close to the thermodynamic potential. Our group has shown in previous

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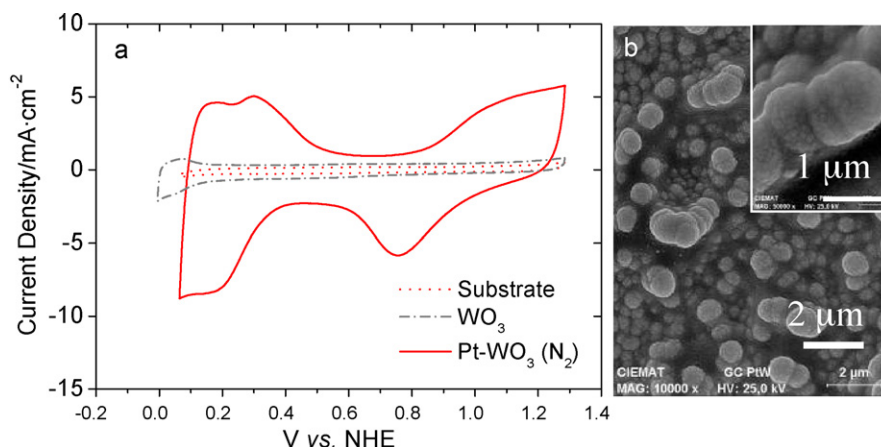


Fig. 1. (a) Cyclic voltammeteries on glassy carbon in 0.5 M H₂SO₄ and N₂ bubbling, corresponding to the substrate prior to electrodeposition (dotted line), electrodeposited WO₃ (dash-dotted line), and electrodeposited Pt–WO₃ (solid line). (b) SEM image of the Pt–WO₃ surface with a detail of the cross section of the electrodeposited layer. Electrodeposition conditions were: 100 sweeps, 0.5 M H₂SO₄, H₂PtCl₆ 0.001 M, Na₂WO₄ 0.01 M, sweep rate 50 mV s⁻¹; room temperature.

communications the possibility of electrodeposition of Pt particles on a porous carbon substrate, and demonstrated good performance in PEM single cell [14,15]. WO₃ can be obtained through combined chemical–electrochemical reactions from either acidic [3,4] or hydrogen peroxide-based Na₂WO₄ solutions [16–18].

Electrodes based on electrodeposited Pt–WO₃ are expected to present several properties that make them interesting for the use in the cathode of PEMFC, such as high stability, high specific surface area and a very low net production of hydrogen peroxide. In this communication, preparation of such electrodes is carried out, followed by testing in single cells. Polarization curves and long term durability (up to 1500 h) are analyzed and compared with standard Pt/C electrodes. Results show that electrodeposited Pt–WO₃ is a suitable material as catalyst for PEMFC, that may decrease platinum requirements. On the other hand, higher durability, beyond 1500 h under variable operation conditions, requires increasing the stability of tungsten oxides. Further research is in progress to improve the performance and durability of the electrodes.

2. Experimental

For electrodeposition of Pt–WO₃ we followed the procedure described by Kulesza and Faulkner [3,4], from fresh solutions 0.001 M H₂PtCl₆ (Aldrich), 0.01 M Na₂WO₄ (Aldrich) in 0.5 M H₂SO₄ (Panreac). The preparation of the electrodes by electrodeposition was carried out in an in-house designed electrochemical cell using a platinum electrode as counter electrode and a mercury sulphate electrode as reference (0.68 V versus NHE). All potentials are given referred to the normal hydrogen electrode, NHE. The substrate for electrodeposition was a commercial gas diffusion layer (microporous carbon on carbon cloth, E-TEK ELAT), previously coated with sprayed commercial carbon black (XC-72 Vulcan) + Nafion (15% wt in the final layer.). The substrate was submitted to an activation procedure in concentrated nitric acid (65% wt) for 5 s, in order to increase its hydrophilic character and electrochemical area for the electrodeposition process [14]. The electrodeposition was carried out on 4 × 4 cm² areas, by application of potential sweeps in different ranges controlled by a potentiostat (Autolab, Eco Chemie). All deposits took place at room temperature (24 ± 2 °C) under continuous bubbling of N₂ to eliminate the oxygen in the solution. After preparation and prior to single cell characterization, the response of each electrode to continuous potential cycling in 0.5 H₂SO₄ was registered. By this means, a first evaluation of electrodes was carried out, including available platinum surface area and stability,

as well as the possible removal of undesirable species from the surface. After having reached a stable signal at this stage, each electrode was tested in single cell.

For single cell characterization of Pt–WO₃ electrodes, the standard procedure included the assembly of membrane electrode assemblies (MEA), 15.2 cm² active area, formed by an electrodeposited electrode (cathode), a commercial (Pemeas, 0.25 mg cm⁻²) Pt/C electrode (anode) and a previously activated Nafion[®] 117 film (membrane). Single cells were mounted using graphite bipolar plates with double channel serpentine flow fields (UDOMI), gold-coated current collectors and heated stain less steel end plates. The start up process and subsequent characterization tests were carried out as described in a previous work [15]. Briefly, once the single cell voltage is stable, it is operated under a constant demand of 1 A, only interrupted when polarization curves or electrochemical active area measurements are carried out. Polarization curves are measured under constant H₂/O₂ 1.5/3 stoichiometry at 1 bar, 80 °C and 100% humidification. Pt active area measurements are based on the well-known hydrogen underpotential deposition on Pt, using different sweep rates (from 5 to 100 mV s⁻¹) and low temperature (303 K), as determined in a previous work [19]. Also, Pt areas were determined by carbon monoxide stripping (CO adsorbed at 0.125 V for 15 min and subsequent potential sweeps at 10 mV s⁻¹, 303 K). The high frequency internal resistance (1 kHz) was continuously measured with a milliohmmeter (HP Agilent 4338th).

SEM images and EDX analysis of electrodeposited electrodes were obtained using a Hitachi 2500 microscope, after deposition of a gold layer by evaporation on the sample in order to enhance the electrical contact with the sample holder. XPS analysis was carried out with a Perkin Elmer PHI 5400 spectrometer using Mg Kα and 1 mm² beam size.

3. Results and discussion

3.1. Basic study of Pt–WO₃ electrodeposition on glassy carbon and GDL

The electrodeposition process of sole WO₃ in acidic solution is a complex process, that seems to involve different faradaic and pH-dependent non-faradaic processes [3,20]. Acidic solutions containing both Pt and W precursors give rise to electrodeposition of both species. Pt deposition is enhanced by the presence of W precursor, as described in the literature [4] and confirmed by electrochemical quartz crystal microbalance experiments [20], and explained by a synergistic effect.

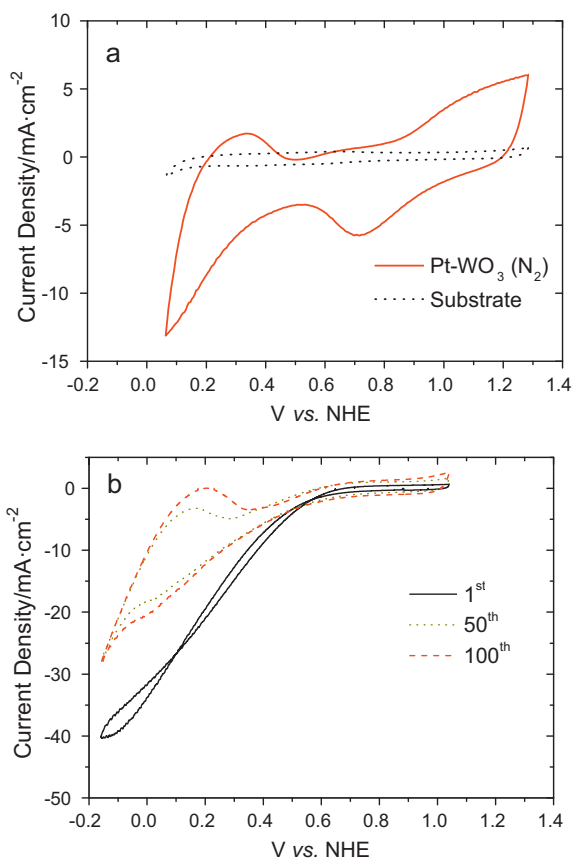


Fig. 2. (a) Cyclic voltammograms on GDL in 0.5 M H_2SO_4 and N_2 bubbling, corresponding to the substrate prior to electrodeposition (solid line) and electrodeposited Pt- WO_3 . (b) Three cycles during Pt- WO_3 electrodeposition. Electrodeposition conditions were: 100 sweeps, 0.5 M H_2SO_4 , H_2PtCl_6 0.001 M, Na_2WO_4 0.01 M, sweep rate 50 mV s^{-1} ; room temperature.

The substrate used for electrode preparation is a pre-treated gas diffusion layer (GDL hereafter), exposing a microporous carbon black surface with Nafion ionomer. This substrate presents a high degree of complexity due to its porous character and composition. For the selection of experimental condition for electrodeposition of Pt- WO_3 we departed from preliminary studies on glassy carbon as a simpler carbonaceous substrate. Fig. 1 summarises the main results of this study. It shows the voltammetric responses in 0.5 M H_2SO_4 of the glassy carbon disk before (dotted line) and after Pt- WO_3 electrodeposition (solid line), as well as after sole WO_3 electrodeposition (dash-dotted line). The presence of Pt after electrodeposition gives rise to a remarkable increase of the active area compared to both the bare glassy carbon disk and electrodeposited WO_3 . Fig. 1.b contains a SEM image of the electrode surface. The thickness of the deposit is around $1 \mu\text{m}$ (see insert) and presents a porous structure composed of metallic Pt and WO_3 , as determined from XPS measurements (not shown). Rotating disk experiments (not shown) demonstrated similar catalytic activity for both pure polycrystalline Pt and Pt- WO_3 , in agreement with the literature [5]. A more detailed description of these basic studies can be found elsewhere [20].

3.2. Electrodes preparation

A carbon cloth substrate coated with carbon black + Nafion[®] was preactivated by direct contact with concentrated HNO_3 for 5 s. After preactivation, a hydrophilic electroactive layer with a thickness of several tens of microns is obtained, whose signal in 0.5 M H_2SO_4 is represented in Fig. 2a (dotted line). The signal after electrodepo-

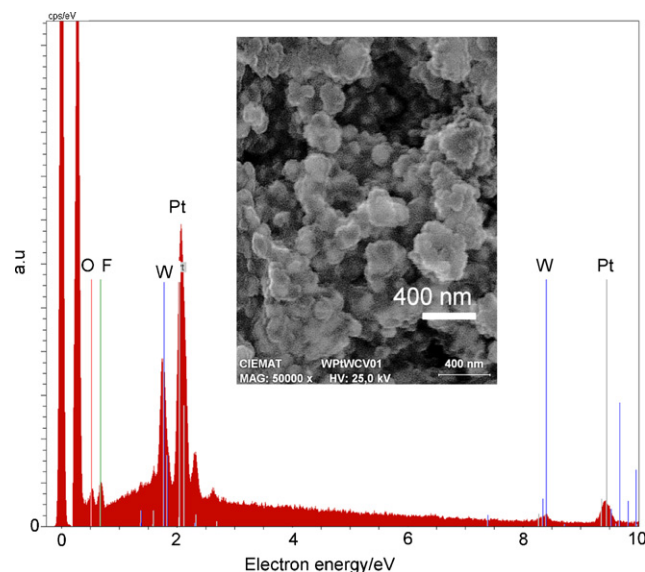


Fig. 3. SEM image of electrodeposited Pt- WO_3 electrode and EDX analysis on the same area.

sition of Pt- WO_3 under N_2 bubbling corresponds to the solid line, which presents close similarity with that measured on glassy carbon (cf. Fig. 1a). Some differences must be attributed to a slightly higher electrical contact resistance of the GDL, and oxygen traces still present in the solution that give rise to a tilted voltammetric response. Fig. 2b shows three electrodeposition cycles, 1st, 50th and 100th. Reduction currents start below 0.8 V, which is mostly the result of the Pt and WO_3 deposition, close to the thermodynamic potential ($V > 0.69 \text{ V}$ for $[\text{Pt}^{4+}] = 1 \text{ mM}$). Some contribution from reduction of residual oxygen must also be expected at these potentials. In successive scans, the signal of oxidation of hydrogen as a result of desorption from the surface of Pt becomes apparent through a wide peak during the anodic cycle, centered at 0.1 V. Simultaneously, reactions 1 and 2 (cathodic sweep) and their reversals (anodic) occur.

SEM images from the surface of electrodeposited Pt- WO_3 electrodes on carbon black (Fig. 3) show carbon black particles coated with a film of Pt- WO_3 . EDX quantitative analysis shows an atomic ratio Pt/W = 3.6, which reflects a preferential Pt deposition, as previously mentioned. EDX measurements also detected important presence of oxygen ($\text{O/W} = 20$), resulting from WO_3 and oxidized carbon surface groups generated upon activation of the substrate. XPS analysis (not shown) showed platinum oxidation state is mostly metallic Pt, while tungsten is mostly present as WO_3 and also as sub-stoichiometric oxides. The state of deposited WO_3 is further analyzed below (see Section 3.3.2 for a further discussion).

3.3. Single cell testing

3.3.1. Polarization curves

Fig. 4 shows polarization curves for two cathodes with different Pt- WO_3 catalyst contents, together with a commercial cathode (Pt/C, 0.25 mg cm^{-2}). The amount of catalyst deposited on the electrodeposited electrodes was estimated from the electrical charge transferred during electrodeposition, assuming it is due entirely to complete Pt reduction ($\text{PtCl}_6^{2-} + 4e^- \rightarrow 6\text{Cl}^- + \text{Pt}$). This assumption is reasonable based on low currents observed for electrodeposition of WO_3 ($< 0.2 \text{ mA cm}^{-2}$) as well as high faradaic efficiency at voltages above 0.1 V, both observed by means of electrochemical balance experiments [20]. Following this procedure, an upper estimation for the amount of Pt content is obtained, which for the case of electrodes in Fig. 4 are $0.25 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ and $0.04 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$.

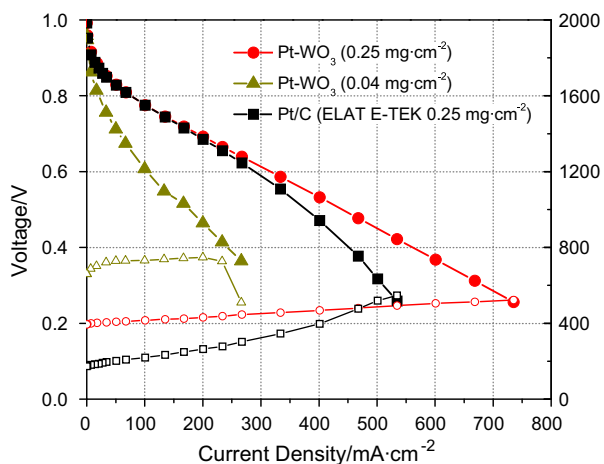


Fig. 4. Polarization curves and 1 kHz internal resistance of two PEM single cells with electrodeposited Pt–WO₃ cathodes with different Pt content, and a cell with commercial Pt/C cathode (0.25 mg cm⁻²). Pt contents were estimated by integration of the electrical charge transferred during electrodeposition, see text. The anode in the three cases was commercial Pt/C, and Nafion® 117 served as membrane. See Section 2 for conditions of measurement.

The polarization curves show a good behaviour of the electrode with the high content of Pt–WO₃ catalyst, similar to the commercial cathode at low currents, indicating a resemblance in catalytic activity, and better at medium and high currents (>200 mA cm⁻²). Further research to explain this fact is ongoing, even though some reasoning can be provided. One possibility may be attributed to improvements in the electrical conductivity of the WO₃ matrix if bronzes and sub-stoichiometric oxides are formed (0.1 ohm cm for WO_{2.75} versus 2×10^5 ohm cm for WO₃) [2], which is probable at cell voltages below 0.4 V (high current demands). Internal resistance also increase with current demand due to less favourable conditions for water management and membrane humidification [21], although the effect for the Pt–WO₃ is significantly lower than for the commercial cathode (Fig. 4), which may reflect the mentioned non-constant electrical conductivity of the WO₃ matrix and probably an improved water management in the electrodeposited electrode.

Further information on Pt–WO₃ cathode behaviour may be obtained by studying single cell response at different pressures. Two polarization curves at different operational pressures (atmospheric and 1 bar) are shown in Fig. 5, in logarithmic scale, for a single cell with Pt–WO₃ cathode. Different pressure conditions pro-

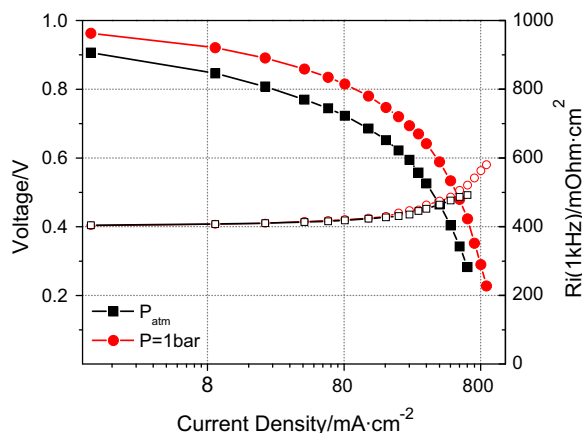


Fig. 5. Polarization curves of single cells with Pt–WO₃ electrodeposited cathode, at two different pressures, atmospheric and 1 bar after 50 h. See Section 2 for conditions of measurement. Internal resistances obtained at 1 kHz are also shown.

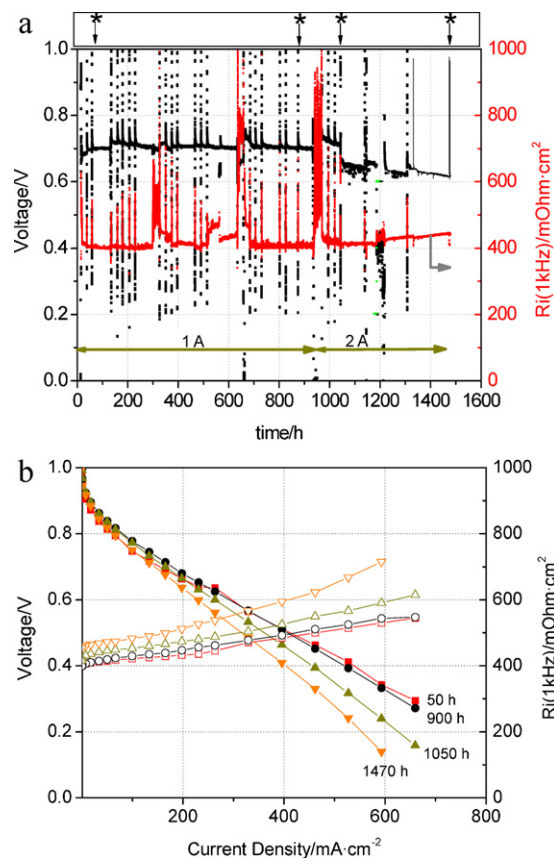


Fig. 6. (a) Voltage and 1 kHz internal resistance as a function of time, for a single cell with an electrodeposited Pt–WO₃ cathode. Steady state operation conditions: constant current demand (as indicated), cell and humidifiers temperature 80 °C, atmospheric pressure, constant flow feeding of 30 ml min⁻¹ of H₂/O₂. (b) Polarization curves taken at indicated operation hours (*) in (a). See Section 2 for conditions of measurement.

voke multiple changes that affect single the cell behaviour, like (i) the equilibrium thermodynamic potential of the cell, (ii) the kinetics of the electrochemical reactions [22], and (iii) mass transfer processes, especially O₂ transport through the cathode. We observe in Fig. 5 a general improvement in the response of the cell when increasing pressure at 1 bar, while the internal resistance at 1 kHz remains almost unchanged up to approximately 600 mA cm⁻². It suggests that mass transport improvement due to a higher pressure becomes relevant above this current density. Electrodeposited Pt–WO₃ electrodes transport properties may be improved by carefully controlling the degree of hydrophilicity of the preactivated porous layer, since a more hydrophilic layer allows an easier penetration of the electrolyte during preparation (and therefore a more homogeneous deposit [4,14]) but, on the other hand, it facilitates partial flooding of the catalyst layer at high currents.

3.3.2. Durability and electroactive area measurements

Fig. 6a shows one long term (ca. 1500 h) durability test performed on single cell with a Pt–WO₃ cathode. The cell was operated at a constant demand of 1 A and atmospheric pressure up to 900 h. Steady state conditions were only interrupted to carry out polarization curves (vertical changes of both the voltage and the internal resistance plots in the figure). It is observed that the voltage reaches a steady value after 100 h, followed by no apparent potential drop up to 900 operating hours. The 1 kHz internal resistance also shows a stable behaviour. At this point, a steady 2 A demand was imposed. Soon afterwards, an undetermined malfunctioning of the cell provoked a steady decline of the cell performance, evident from the

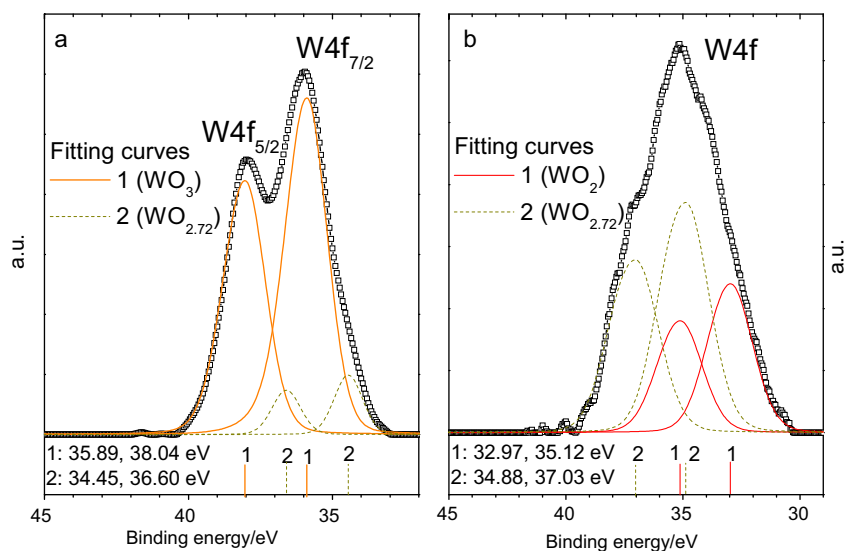


Fig. 7. XPS spectra of W4f signals for a Pt-WO₃ electrode (void symbols). (a) Prior to single cell testing and (b) after testing. Deconvolutions of the experimental data are represented as solid lines.

continuous voltage drop and internal resistance increase. Actually, a change from 1 to 2 A was expected to reduce carbon corrosion due to lower cathodic voltage, while no significant impediment for proper water management or oxygen transport was expected, on the light of polarization curves in Figs. 4 and 5. Fig. 6b includes polarization curves recorded after different operation times (^{*} in Fig. 6a). It is clear no significant degradation of the electrode took place for the first 900 h. Afterwards, the increase of the cathodic ohmic resistance seems to be the predominant cause for its performance degradation, since no clear differences can be detected at low currents (where polarization caused by activation predominate), as confirmed by the corresponding curves at 1050 and 1420 h.

Accelerated degradation of Pt-WO₃ appears to take place upon increasing steady state current demand. Pereira et al. [6] observed degradation on single cell experiments for anodic Pt-WO₃ electrodes due to an increase of the membrane's ohmic resistance attributed to WO₃ passing through the membrane. In order to study the possible cause of electrode degradation, XPS measurements were carried out prior (Fig. 7a) and after (Fig. 7b) cell testing. It is shown that for a fresh electrode, WO₃ is the predominant tungsten species on the surface of the electrode (89.5% according to deconvolution of the peaks) whereas sub-stoichiometric oxides also appear as a consequence of the preparation method (10.5% WO_{2.72}). After testing, the predominant tungsten species are sub-stoichiometric oxides (62.8%) while a significant portion of WO₂ arises (37.2%). These results appear to show that formation of the soluble δ -oxide (WO₂) takes place on aged electrodes when sub-stoichiometric oxides are formed. WO₂ dissolution is possible in the cathode acidic environment [23]. Its penetration into the membrane may cause the observed increase in internal resistance and cell degradation. As a consequence, the rate at which WO₂ is formed may be determinant for the durability of Pt-WO₃ electrodes.

Recent studies have reported enhanced stability for cathodic Pt-WO₃ electrodes in single cell prepared by chemical methods [11,12]. There were detected significant losses due to higher ohmic resistance and lower mass activity than a commercial Pt/C electrode as well as modest mass transport properties. Our electrodes also showed high ohmic resistance but similar mass activity respect to the commercial one and good mass transport properties up to 600 mA cm⁻². One could expect that the nature of the electrodepo-

sition process may reinforce the interactions between Pt, the WO₃ matrix and the carbon support. Further research is ongoing in order to characterize these interactions. The catalytic activity for H₂O₂ decomposition of tungsten bronzes is expected to be a key reason for improved durability of cathodic PEMFC electrodes, as recently reported in the literature [11]. This process does not depend on the preparation method but on the nature of Pt-WO₃ material, thus, may be present in our electrodes. However, WO₃ could also act as a partial blocking of oxygen access to carbon black particles (covered by the tungsten oxide), which is a well-known catalyst for H₂O₂ production [24]. Information about the relative importance of these effects may be extracted from voltammetric responses of the electrodes, as described below.

Measurement of underpotential deposited hydrogen provides information about the evolution of the catalyst layer electroactive area during the long term experiment. Fig. 8 contains cyclic voltammograms in N₂ atmosphere after 700 and 1500 h (end of the experiment). Below 0.4 V, several processes: hydrogen underpotentially deposited and desorbed from Pt as well as tungsten bronzes and sub-stoichiometric oxides formation and decomposition (reactions (1) and (2)) are superimposed, so it is not possible to distinguish the proportion of WO₃ leaving the catalyst layer or

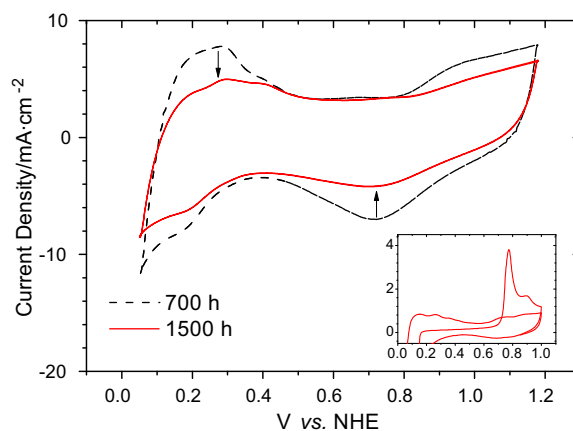


Fig. 8. Cyclic voltammograms of the Pt-WO₃ cathode measured in single cells at two different operation times. Inset: CO stripping peaks after 1500 h. Sweep rates 10 mV s⁻¹. See Section 2 for the rest of conditions.

being decomposed. On the other hand, double layer charge currents (between 0.5 and 0.8 V in the anodic scans) remain almost unchanged with time, revealing that the electroactive area remains. It suggests a low moiety of electroactive carbon black covered by WO_3 , as supported by the evidence of preferential Pt deposition (see Section 3.2) and reinforced during the experiment by the significant formation of soluble WO_2 (Fig. 7). As a consequence, the effect of the WO_3 matrix as a physical blockage for O_2 access to carbon seems negligible in these electrodes. The insert in Fig. 8 contains the oxidation of adsorbed CO in N_2 atmosphere (first and second scans after 1500 h). A double oxidation peak is observed, in accordance with the reported results from Maillard et al. [7]. They observed an additional peak around 0.55 V, absent in our case, attributed to CO oxidation at the Pt particles- WO_x interphase. Pt active areas calculated from hydrogen desorption (therefore neglecting contributions from reactions 1 and 2) and CO stripping yielded results within 10%, as usually observed on Pt/C electrodes [16,25], suggesting a low electrochemical response of the WO_3 matrix.

These results appear to show that platinum and part of the WO_3 matrix are lost with time, attributed to soluble WO_2 formation. A decrease of the Pt active area is also apparent from lower currents obtained at Pt oxides formation and reduction potential ranges (Fig. 8, from 0.8 V in the anodic scan and around 0.7 V in the cathodic, respectively).

4. Conclusions

Pt- WO_3 electrodes were prepared by electrodeposition on pre-treated GDLs and subsequently tested in a PEM single cell as cathodes. Characterization of electrodes revealed preferential Pt electrodeposition. Electrodeposited electrodes show good performance in single cell. A good stability was obtained up to 1500 h, with no apparent degradation of the electrode until 900 h. Some of the reasons for performance degradation are Pt electroactive area decrease and partial dissolution of WO_3 through formation of soluble WO_2 over the operation time.

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