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Article

Spin-Coated *vs.* Electrodeposited Mn Oxide Films as Water Oxidation Catalysts

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Abstract: Manganese oxides (MnO_x), being active, inexpensive and low-toxicity materials, are considered promising water oxidation catalysts (WOCs). This work reports the preparation and the physico-chemical and electrochemical characterization of spin-coated (SC) films of commercial Mn₂O₃, Mn₃O₄ and MnO₂ powders. Spin coating consists of few preparation steps and employs green chemicals (*i.e.*, ethanol, acetic acid, polyethylene oxide and water). To the best of our knowledge, this is the first time SC has been used for the preparation of stable powder-based WOCs electrodes. For comparison, MnO_x films were also prepared by means of electrodeposition (ED) and tested under the same conditions, at neutral pH. Particular interest was given to α-Mn₂O₃-based films, since Mn (III) species play a crucial role in the electrocatalytic oxidation of water. To this end, MnO₂-based SC and ED films were calcined at 500 °C, in order to obtain the desired α-Mn₂O₃ crystalline phase. Electrochemical impedance spectroscopy (EIS) measurements were performed to study both electrode charge transport properties and electrode–electrolyte charge transfer kinetics. Long-term stability tests and oxygen/hydrogen evolution measurements were also made on the highest-performing samples and their faradaic efficiencies were quantified, with results higher than 95% for the Mn₂O₃ SC film, finally showing that the SC technique proposed here is a simple and reliable method to study the electrocatalytic behavior of pre-synthesized WOCs powders.

Keywords: water oxidation; electrodeposition; manganese oxides films; polyethylene oxide; electrochemical impedance spectroscopy

1. Introduction

One of the most promising approaches for the exploitation of solar energy is the production of fuels by means of photocatalytic processes. Water splitting (WS) is an interesting technology to transform solar energy and to store it in the form of green chemicals or fuels, such as oxygen and hydrogen. The overall reaction (1) is the sum of the two half-reactions of oxidation (2) and reduction (3):



of increasing the adhesion between the film and the substrate. Only the MnO₂ sample (amorphous) was calcined at higher temperature (*i.e.*, 500 °C), in order to induce changes in the crystalline phase to α-Mn₂O₃ [30]. The samples are named considering the method used to achieve the film and the crystal phase. The MnO₂ sample will therefore be referred to as Mn₂O₃-SC-TT.

2.3. Films Prepared by Electrodeposition

The preparation of the electrodeposited films was adapted from the literature [22]. A typical three-electrodes cell, with a Pt wire as counter electrode, Ag/AgCl as a reference electrode and a FTO-coated glass substrate as the working electrode, was used for the electrodeposition of amorphous MnO_x films. The FTO substrates were previously cleaned with piranha solution (H₂SO₄:H₂O₂ = 3:1, *v/v*) and masked to leave an active surface of 2 × 2 cm². The electrodeposition was performed at constant current of 1 mA for 3 different deposition times *t* (ED1, ED5 and ED10 correspond to *t* = 1 min, 5 min and 10 min, respectively), in a solution containing 0.1 M Na₂SO₄ as supporting electrolyte and 0.1 M Mn(CH₃COO)₂·4H₂O as Mn precursor. The pH was adjusted to 5.7 with acetic acid. The films were tested both as-synthesized and after calcination at 500 °C for 2 h (with a heating rate of 5 °C·min⁻¹) in calm air, with the aim of forming the crystalline phase α-Mn₂O₃ (samples referred as ED*t**c*, where *t* stays for the deposition time and *c* for the calcination step).

2.4. Characterization Techniques

X-ray diffraction (XRD) patterns of the films were collected on an X'Pert Phillips diffractometer using Cu Kα radiation = 1.541874 Å (20–60 2θ range; step width = 0.02 degree; time per step = 2 s) and indexed according to the Powder Data File database (PDF 2000, International Centre of Diffraction Data, Philadelphia, PA, USA). The morphology of the samples was investigated by Field Emission Scanning Electron Microscopy (FE-SEM) (ZEISS, Oberkochen, Germany) on a Zeiss Supra 40 instrument. Cross-section images were used to determine the average thickness of the films. UV-Visible transmittance spectra were recorded by using a UV-Vis Varian Cary 5000 spectrophotometer (Agilent Technologies, Inc., Santa Clara, CA, USA).

2.5. Electrochemical Measurements

Electrochemical measurements were run with a standard three-electrodes setup in a lab-made glass cell with an Ag/AgCl (3 M KCl) electrode as reference electrode and a Pt wire as counter electrode. The measurements were recorded by using a multichannel VSP potentiostat/galvanostat (BioLogic), equipped with EC-Lab v. 10.1x software for data acquisition. The reported potentials are referred to the reversible hydrogen electrode (RHE). The measured potentials *vs.* the Ag/AgCl reference electrode were converted to the RHE scale by using the Nernst Equation: $E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl}^0 + 0.059 pH$. E_{RHE} is the converted potential *vs.* RHE, $E_{Ag/AgCl}$ is the experimental potential measured against the Ag/AgCl reference electrode, and $E_{Ag/AgCl}^0$ is the standard potential of Ag/AgCl (3 M KCl) at 25 °C (*i.e.*, 0.210 V). The catalytic activity of MnO_x films was tested at pH = 7.0 in 0.1 M sodium phosphate buffer. Cyclic voltammeteries (CVs) were performed in the range between 0.6 and 2.0 V *vs.* RHE with a sweep rate of 20 mV·s⁻¹. Current density was calculated by considering the geometrical area of the FTO substrate covered by the MnO_x film (~4 cm²).

For Tafel plot analysis, current density was recorded stepwise between 1.4 V and 2.0 V *vs.* RHE until reaching quasi-stationary currents. Therefore, the electrode potential was increased by 40 mV steps and held for 5 min. The potential was corrected for the ohmic drop, hence, impedance spectra were recorded at every potential/current step at 10 kHz with a modulation amplitude of 20 mV in order to determine the ohmic resistance of the solution ($R_s \sim 40 \Omega$). The overpotential (η) values reported in both Tafel plot and Table 1 were calculated as follows: $\eta = E_{RHE} - E_{RHE}^0 - iR$, where E_{RHE}^0 is the standard potential of the water splitting reaction (~1.23 V) and *i* is the current. EIS curves were recorded using the same potentiostat described above from 0.1 Hz to 0.5 MHz, with an alternating current (AC) amplitude of 20 mV at different applied potentials (*i.e.*, 1.0 V, 1.2 V and 1.4 V *vs.* Ag/AgCl).

Oxygen and hydrogen evolutions were measured by a Varian 490 micro-GC equipped with a Molsieve column during chrono-amperometry test at a fixed potential of 2.0 V *vs.* RHE, after purging of the cell with a continuous Ar flow for 1 h. An Argon flow rate of 25 Nml·min⁻¹ was used in order to carry the evolved O₂ and H₂ gases from the cell to the micro-GC, while the solution was maintained under continuous stirring to increase the mass transfer of the dissolved gases to the gaseous media.

3. Results and Discussion

3.1. Spin-Coated Samples

The SC method was initially tested with as-purchased micrometric Mn₂O₃ and Mn₃O₄ powders (average particle size ~2 to 5 μm). Nevertheless, the large particle size (Figure S1 in the Supplementary Materials) led to a poor adhesion of the catalyst to the substrate, causing some material detachment during electrochemical tests, with a consequent drastic decrease in catalytic activity after few voltammetry cycles. Therefore, both Mn₂O₃ and Mn₃O₄ powders were ball-milled in order to reduce their particle size [30]. SC of ball-milled samples led to a more effective adhesion of the film on the FTO substrate, and allowed for better particle interconnection. In contrast, the commercial MnO₂ powder was characterized by a heterogeneous particle size distribution, and it was used without any modification. Indeed, during the SC procedure only the smaller particles adhered to FTO (the larger ones being removed by centrifugal force), yielding to stable films.

The morphology of SC films of the commercial MnO_x powders is shown in the FE-SEM images in Figure 1. The MnO₂ film is constituted of nearly spherical nanoparticles with average diameter of 20 nm. Concerning Mn₂O₃ and Mn₃O₄ films, the particles show extremely variable morphology and size; however, it must be stressed that ball-milling was effective in decreasing their size from the original micrometric size (2 to 5 μm) to 30 ÷ 170 nm (Mn₂O₃) and 70 ÷ 400 nm (Mn₃O₄). With all the considered samples, particles are well-distributed on FTO surface by forming a continuous coverage of the substrate. The film thickness, as measured by cross-section FE-SEM, lies in the 500 ÷ 1500 nm range for all the SC samples (Figure S2 in Supplementary Materials).

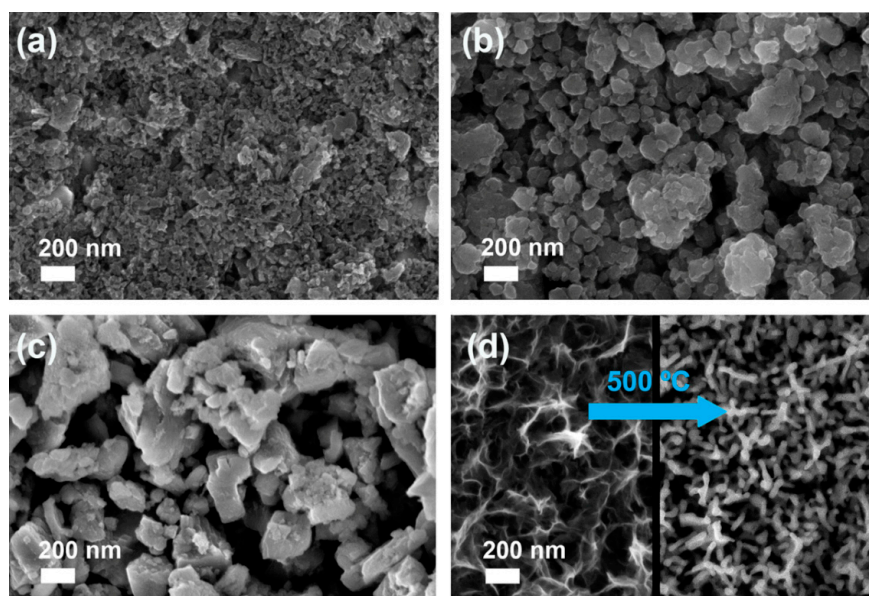


Figure 1. FE-SEM images of a top view of MnO₂ (a); Mn₂O₃ (b) and Mn₃O₄ (c) SC films after annealing at either 500 °C or 400 °C; (d) FE-SEM images of a top view of the ED film: as-prepared sample (left image) and annealed at 500 °C (right image).

According to our previous study [30], the calcination of the MnO₂ SC film at 500 °C (Mn₂O₃-SC-TT) resulted in the formation of an α-Mn₂O₃ crystalline phase, as confirmed by the

XRD pattern (curve c, Figure 2). The structural reorganization apparently did not affect particle morphology, but led to a decrease of SSA (from 98 to 20 $\text{m}^2 \cdot \text{g}^{-1}$) [30]. In contrast, the crystalline phases of both Mn_2O_3 and Mn_3O_4 powders were not affected by the thermal treatment at 400 °C performed on their respective SC films (*i.e.*, Mn_2O_3 -SC and Mn_3O_4 -SC). Indeed, the XRD pattern of Mn_2O_3 -SC film (curve b in Figure 2) evidenced the main peaks (at 2θ of about 23.2° and 32.9°) corresponding to the (211) and (222) crystalline planes of bixbyite. Similarly, the XRD pattern of Mn_3O_4 -SC film (curve a in Figure 2) showed the typical diffraction peaks of hausmannite.

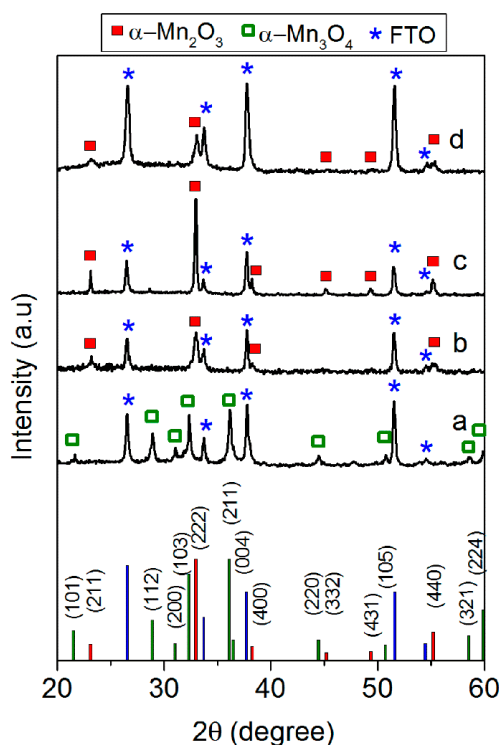


Figure 2. XRD patterns of Mn_3O_4 -SC (a); Mn_2O_3 -SC (b); Mn_2O_3 -SC-TT (c) and ED5c (d) films. Indices of each crystalline phase found in the XRD patterns are reported in the bottom section of the figure.

The catalytic activity of the MnO_x films was evaluated by using them as anodes in the electrochemical WS reaction, with Na-Phosphate buffer as electrolyte (pH = 7.0). The multiple cyclic-voltammetry (CV) curves in Figure 3a evidence the current density behavior of the different materials as a function of the applied potential: the adopted SC procedure yielded to films with good stability, since the 10 CV cycles were highly reproducible for all the samples studied.

Figure 3. Electrochemical characterization of the SC-films: cyclic voltammograms (a) and Tafel plots (b) in 0.1 M Na-phosphate buffer (pH = 7.0). Potential (E) is referred to the RHE (see Section 2.5).

respectively. In addition, similarly to what is observed for the SC films, the Tafel plots of the ED films show an inflection point, the position of which moves towards lower η at increasing deposition time. A linear η vs. $\log(j)$ dependency in the 470 \div 670, 390 \div 550 and 315 \div 430 mV overpotential range, and the corresponding Tafel slopes of 130, 148 and 105 mV \cdot dec $^{-1}$ are observed with ED1, ED5 and ED10, respectively.

After calcination (samples are referred as ED t c, where c stays for the calcination step, see Figure 4b), the Tafel slopes of both ED1c and ED5c were lowered to 120 and 115 mV \cdot dec $^{-1}$, respectively, whereas that of ED10c increased to 130 mV \cdot dec $^{-1}$. The thermal treatment is particularly beneficial for intermediate deposition time (*i.e.*, for ED5c), as shown by the widening towards lower η of the linear portion of the Tafel slope (270 \div 500 mV), and by the consequent decrease in η required to obtain a 0.1 mA \cdot cm $^{-2}$ current density (*i.e.*, 470 mV). Interestingly, such an effect is not likewise marked for ED10c, suggesting that there is a limit in the α -Mn $_2$ O $_3$ film thickness beyond which the whole exposed surface is not effectively exploited. Curiously, ED5c showed a film thickness of the same order of those obtained by SC method (Figure S2).

The Tafel plots of ED5c and ED10c practically overlap at high potentials, achieving 0.9 mA \cdot cm $^{-2}$ current density at $\eta = 800$, *i.e.*, 30% higher than those obtained by the SC films at the same potential. Similarly to what observed for the SC films, the reaction rate with ED films (both as-deposited and calcined) at high overpotential does not increase linearly with the applied potential, probably due to a limitation in the electronic transport within the film.

In conclusion, the optimal compromise between the MnO $_x$ deposited amount and the activity in WO reaction was obtained with the sample ED5c. For this reason, that electrode was selected for a more detailed study (*i.e.*, EIS and oxygen/hydrogen evolution measurements), together with the SC films having the same α -Mn $_2$ O $_3$ phase and similar thickness.

3.3. Charge Transfer and Transport Mechanisms in Mn $_2$ O $_3$ -Based Films

The spin-coated Mn $_2$ O $_3$ -SC and Mn $_2$ O $_3$ -SC-TT and the electrodeposited ED5c films were characterized by EIS at different applied potentials (higher than the on-set potential) at which the electrodes exhibit a current density greater than 0.01 mA \cdot cm $^{-2}$, with the aim of comparing their charge transfer and transport properties. EIS results at 1.6, 1.8 and 2.0 V vs. RHE (corresponding to about 380, 530 and 640 mV of overpotential, respectively) are reported in Figure 5 in the form of Bode plots, which show both phase and modulus ($|Z|$) of impedance vs. frequency. Nyquist plots are also reported in Figure S5 of the Supplementary Materials for the sake of completeness.

Concerning the phase spectra in Figure 5a, two features are related to the two different processes occurring in the analyzed electrochemical system: the high frequency peak centered at about 100 Hz, associated with the charge transport properties of the electrode material, and the lower frequency peak, associated with the charge transfer at the electrode/electrolyte interface [28,35]. For all the samples, in the low frequency region (<100 Hz) impedance decreases with the increase of the applied potential, because of an enhancement of the reaction kinetics, which is induced by the electrical forces, but depending on the surface properties of the electrode materials. The same behavior is observed by a reduction of the semicircles diameter at increasing potential values in the Nyquist plots of Figure S5. Indeed, if the $|Z|$ values at 0.1 Hz are considered, the charge transport resistance for ED5c decreases of about four times when passing from 1.6 to 2.0 V vs. RHE, whereas for the SC films it is halved. Furthermore, it is evident that the ED5c film retains better charge transport properties than the SC samples, as lower $|Z|$ values are obtained at *ca.* 100 Hz for all the applied potentials. Such results are in agreement with the CV analysis and Tafel plots, and indicate that both nanostructuring and good adhesion of the ED film (which was directly grown on the FTO-glass substrate) play an important role in the increase of the current density with the applied potential. Furthermore, EIS analysis explains the higher electrocatalytic activity of ED5c electrodes at high potential (*i.e.*, 2 V vs. RHE).

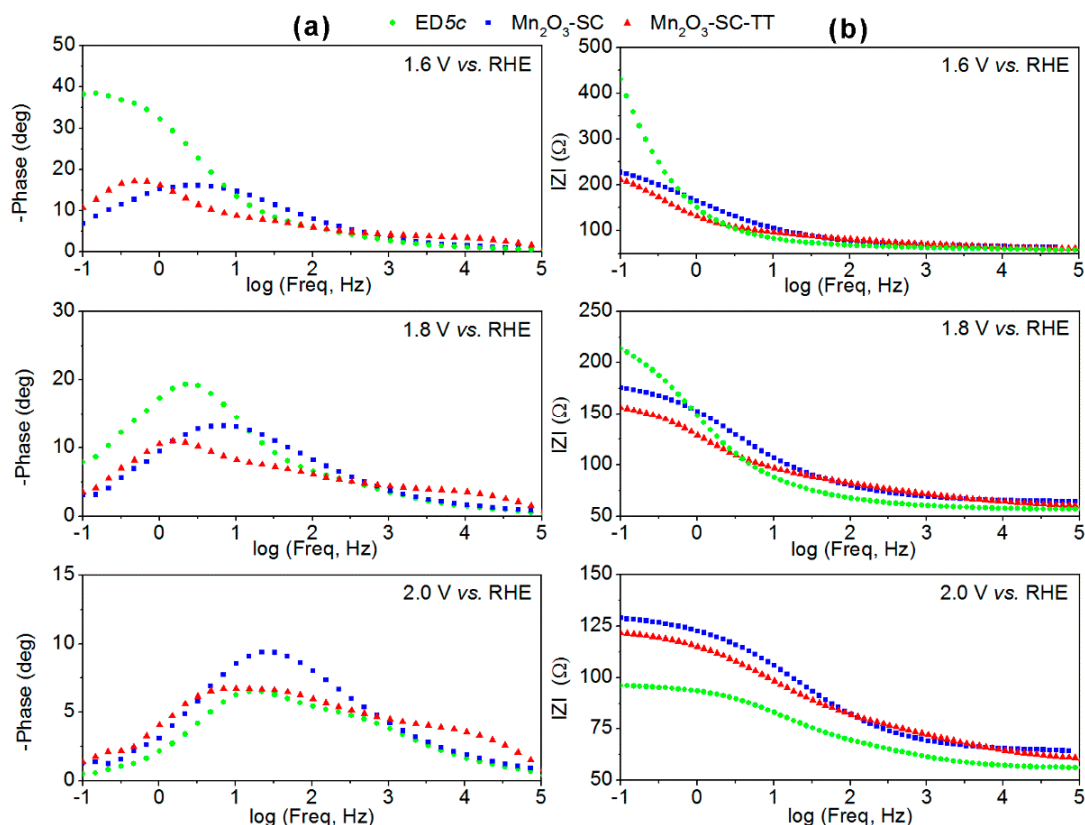


Figure 5. Bode plots representing (a) phase and (b) module of impedance acquired during EIS measurements by using the α -Mn₂O₃-based electrodes at 1.6, 1.8 and 2.0 V vs. RHE.

It is of note that at low overpotential (*i.e.*, 380 mV or 1.6 V vs. RHE) the SC films presented faster kinetics at the electrodes-electrolyte interface, showing half of the charge transfer resistance with respect to the ED film. Such result suggests that the SC films retain a more defined crystalline structure and, therefore, have better-defined electrocatalytic properties at low applied potentials than the ED film. On the other hand, the highly heterogeneous adhesion to the substrate and the interparticles contact within SC films have an influence on the maximum current densities that can be achieved.

Finally, the Mn₂O₃-SC-TT film apparently evidenced faster kinetics than the Mn₂O₃-SC film, as observed from slightly lower $|Z|$ values. Nevertheless, its higher phase values in the high frequency region (\sim 1000 Hz) indicate a pseudo-capacitive effect and suggest that some residual MnO₂ phase could still be present in this sample.

3.4. Oxygen/Hydrogen Evolution Measurements

The α -Mn₂O₃-containing electrodes (Mn₂O₃-SC, Mn₂O₃-SC-TT and ED5c) were selected and tested under the same chrono-amperometric conditions (*i.e.*, 2.0 V vs. RHE for 1 h) in order to verify their long-term stability and their faradaic efficiencies in O₂ and H₂ evolution. Figure 6 shows the O₂ and H₂ evolutions and the current density observed for each film on the time course of the experiment. As expected by the reaction stoichiometry, the molar amount of H₂ produced doubles that of O₂ within the experimental sensitivity of the gas-chromatographic analysis. Both SC films show similar performances, in correspondence with the Tafel plots and CV curves. A summary of the electrocatalytic tests and activity indicators of these three films is also reported in Table 1. The highest O₂ evolution was obtained with ED5c, in agreement with the higher current densities. It is worth noting that the morphologies of the ED film and the SC film are different. In the first case, the MnO_x materials were grown forming a well-connected network of nanosheets that after calcination sintered to form interconnected nanorods, whereas the SC method yielded to non-highly associated particles. Therefore,

it is expected that particles boundaries can generate an additional obstacle to charge transport in the SC films, as discussed above from the EIS data analysis, thus influencing their performance. The highest faradaic efficiencies (95% and 97% for O₂ and H₂ production, respectively) were measured with Mn₂O₃-SC, probably due to the higher crystallinity of the starting α -Mn₂O₃ powder material. In addition, in agreement with the previous results, the sample Mn₂O₃-SC-TT reported the lowest O₂ and H₂ faradaic efficiencies, confirming the incomplete transformation of the MnO₂ phase.

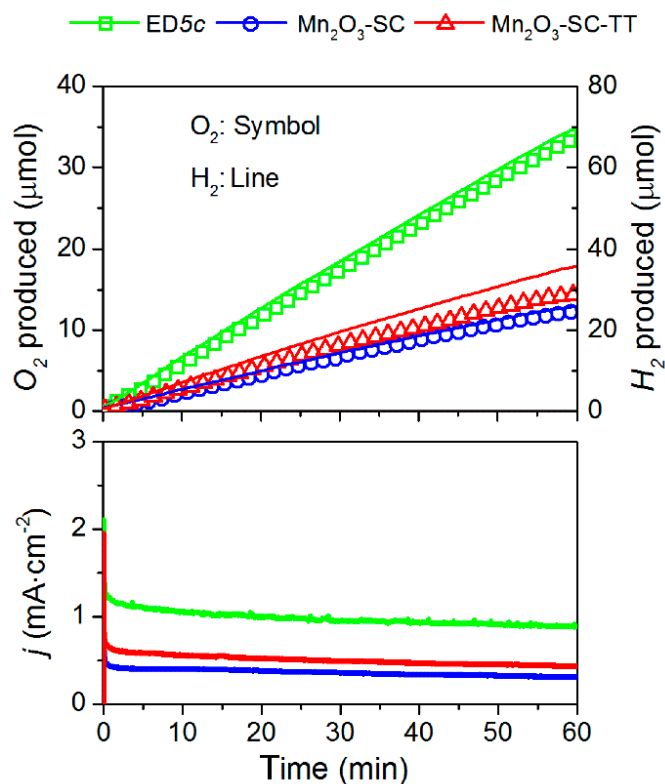


Figure 6. Oxygen and hydrogen evolutions under an applied potential of 2.0 V *vs.* RHE. Time course of the O₂ and H₂ production analyzed by a micro-GC (**up**) and of the measured current densities (**bottom**).

4. Conclusions

This work compares the effectiveness of spin-coating (with polyethylene oxide as a binder) and electrodeposition as techniques for the preparation of stable MnO_x-based electrodes active in the water oxidation reaction. Though spin-coating requires previous ball-milling of the catalyst in order to obtain stable and active films from originally microstructured powders, it leads to uniform films and allows removal of polyethylene oxide at mild temperatures (as low as 200 °C), and therefore it results a method potentially suitable to obtain electrodes of different types of catalysts.

Electrodeposition allows films to be obtained with nanostructured morphology, but the catalyst is amorphous, its catalytic activity depending on both deposition time and calcination. Concerning water oxidation, electrodeposited films indeed reached activities comparable (or higher) with respect to spin-coated films only after calcination at 500 °C, a treatment leading to the formation of α -Mn₂O₃, the active phase in spin-coated films as well. Calcination was particularly effective at intermediate electrodeposition times, but not at longer deposition times, suggesting that there is an upper limit to the thickness of the α -Mn₂O₃ film above which the overall exposed surface is not actually exploited.

Electrochemical impedance spectroscopy showed that electrodeposited films have better charge transport properties compared to spin-coated ones, as shown by a higher electrocatalytic activity of the former at high overpotential. On the other hand, at low overpotential, spin-coated films presented faster kinetics at the electrode/electrolyte interface, showing half of the charge transfer resistance

compared to electrodeposited ones. Such result suggests that spin-coated films have better-defined electrocatalytic properties (at low applied potentials), likely due to the higher crystallinity of the pre-formed commercial catalysts. As a consequence, the spin-coating procedure presented here appears to be a simple and reliable method to fabricate electrodes with pre-synthesized powders of water oxidation catalysts.

Supplementary Materials: The following are available online at www.mdpi.com/1996-1944/9/4/296/s1. Figure S1: Cross-section FE-SEM image of a spin-coated film made with a non-ball-milled Mn_2O_3 powder; Figure S2: FE-SEM cross-section images of the films prepared by spin-coating of MnO_2 (a); Mn_2O_3 (b) and Mn_3O_4 (c) powders; as-made electrodeposited 5-min film (d); Figure S3: UV-Vis transmittance spectra of the electrodeposited films: as-made (continuous line) and calcined at $500\text{ }^\circ\text{C}$ (dotted line); Figure S4: Photographs of the as-made films prepared by electrodeposition at different deposition times; and Figure S5: Nyquist plots of the EIS measurements acquired using the $\alpha\text{-Mn}_2\text{O}_3$ -based electrodes at 1.6, 1.8 and 2.0 V vs. RHE.

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Author Contributions: Simelys Hernández ideated the work and, in collaboration with Diego Pugliese, developed and optimized the recipe for the fabrication of the films by spin-coating technique. Sara Varetto contributed to the electrodes preparation. She and Carminna Ottone carried out the electrochemical measurements. Marco Fontana performed the morphological characterization. Marco Armandi characterized the physicochemical properties of the materials and supervised the work of Sara Varetto together with Simelys Hernández, Guido Saracco and Barbara Bonelli gave advises on the experimental procedure and critically contributed to the interpretation of the results. All authors discussed and analyzed the results, contributed to writing and approved the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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