

Article

Oxygen Reduction Reaction Electrocatalysis in Alkaline Electrolyte on Glassy-Carbon-Supported Nanostructured Pr_6O_{11} Thin-Films

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Abstract: In this work, hierarchical nanostructured Pr_6O_{11} thin-films of brain-like morphology were successfully prepared by electrostatic spray deposition (ESD) on glassy-carbon substrates. These surfaces were used as working electrodes in the rotating disk electrode (RDE) setup and characterized in alkaline electrolyte (0.1 M NaOH at 25 ± 2 °C) for the hydrogen evolution reaction (HER), the oxygen evolution reaction (OER), and the oxygen reduction reaction (ORR) for their potential application in alkaline electrolyzers or in alkaline fuel cells. The electrochemical performances of these electrodes were investigated as a function of their crystallized state (amorphous versus crystalline). Although none of the materials display spectacular HER and OER activity, the results show interesting performances of the crystallized sample towards the ORR with regards to this class of non-Pt group metal (non-PGM) electrocatalysts, the activity being, however, still far from a benchmark Pt/C electrocatalyst.

Keywords: electrostatic spray deposition; Pr_6O_{11} ; non-Pt group metal (non-PGM); electrocatalyst; alkaline electrolyte; oxygen reduction reaction

1. Introduction

With the development of renewable electricity—a necessity to face the present fossil energy crisis and limit the harmful emissions of related greenhouse gases—the means to store this energy upon production peaks and to release it upon demand peaks is mandatory [1]. One very efficient manner to do so lies in the so-called hydrogen economy, where H_2 (and O_2) is produced in water electrolyzers (acidic [2], alkaline [3], or, if necessary, with advanced physical procedures to boost the reactions [4]), stored, and then converted back to water and electrical energy in fuel cells. The so-called unitized regenerative fuel cells (URFC) [5,6], as well as photocatalytic water-splitting devices [7,8] are also convenient means to do so. In these systems, the reactions of oxygen reduction (ORR) and oxygen evolution (OER) limit the operation in fuel cell and electrolyzer mode, respectively, whatever the pH of operation. Moreover, the electrocatalysts that can sufficiently and durably accelerate these reactions in acidic (proton-exchange membrane) conditions are based on platinum group metals (PGM) [9,10], which conveys dramatic issues in terms of availability and cost of the electrodes. As a result, the sustained hydrogen cycle might only be viable for alkaline systems for which the potential choice of more available and less costly non-noble electrocatalysts is greater (and simply possible) [11]. There are extremely vast numbers of potential non-PGM electrocatalysts for the ORR [12–18] and OER [19–28] (these examples being by-no-means comprehensive), and metal oxides in the perovskite structure play a large role in this hot area, owing to their non-negligible activity

for the oxygen reduction and evolution reactions, and the extremely large variety of components available [6,11,29–32]. Perovskite oxides, usually based on rare-earth component(s), are usually not sufficiently electron-conductive on their own to exhibit sufficient performances, and they are, therefore, generally used in composite electrodes while including some carbon additive [32–36]. Addition of carbon is usually very positive for the ORR [37–41] and results from a combination of effects like (i) an increase of electronic conductivity of the active layer, (ii) a bifunctional mechanism in which carbon enhances hydrogen peroxide formation, the latter being decomposed/reduced on the perovskite oxide, and (iii) a change of the perovskite electronic and/or crystalline structure(s) promoted by carbon [32,35]. On the contrary, adding carbon is detrimental for the OER as a result of its poor durability in operation [32,37,38]. Nevertheless, very interesting performances have been reached to date, both for the ORR and OER on this class of materials [31,42], but it is unclear from these studies what the intrinsic activity of the perovskite component is. More recently, carbon-free active layers based on perovskite oxides have been described and tested, which shed light on the intrinsic electrocatalytic properties of the electrocatalysts, and highlighted the role of their electronic conductivity and lattice strain, two parameters which need a certain balance to reach high ORR and OER activity [43]. The importance of the crystalline nature of the perovskites has been ascertained, with smaller crystals yielding larger ORR activity [44]. The influence of the facets has also been put forth [45] as well as the crystalline versus amorphous nature of the oxide [46,47], but in these cases, composite electrodes using carbon additives were used.

Rare-earth oxides are also popular in the field of high-temperature solid-state electrochemistry and in particular for solid oxide fuel cells (SOFCs). For example, Pr_6O_{11} has been reported to enhance electrochemical ORR performance when used as an additive in composite oxygen electrodes: Pr_6O_{11} -infiltrated $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (LNF) electrodes exhibited improved performance over LNF ($\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$) electrodes, as reported by Chiba et al. [48] and Ding et al. [49]. More recently, polarization resistances as low as $0.026 \, \Omega \, \text{cm}^2$ at $600 \, ^\circ\text{C}$ were reported for a pure Pr_6O_{11} columnar-type cathode prepared by electrostatic spray deposition (ESD) [50]. The ESD technique is a film-coating method based on the principle of electrostatic atomization [51]. First, a positive high voltage is applied to the stainless steel nozzle from which positively-charged droplets of a solution of precursors are generated. Then, they are directed to the grounded substrate thanks to the electrical field. Finally, the size of the droplets at the moment of impact on the heated substrate and the combined effects of relative spreading and drying rates will determine film morphology. A schematic drawing of the ESD system has been presented in Reference [52]. This innovative process is a low-cost and versatile technique to elaborate a wide variety of oxide materials with large reproducibility and controlled microstructures [50,53–57].

In the present contribution, Pr-based oxides (Pr_6O_{11}) have been prepared for the first time as thin-films on glassy-carbon substrates by ESD; these electrodes, prepared without any addition of carbon black additive, were tested for their activity of hydrogen and oxygen evolution reactions (HER and OER), and oxygen reduction reactions (ORR) in dilute alkaline electrolyte. The oxide crystallinity, in particular, has been evaluated by comparing the fate of amorphous and crystalline Pr_6O_{11} .

2. Results and Discussion

2.1. Microstructural Characterization and Elemental Analysis

The microstructures of the films deposited with a flow rate of $Q = 1.5 \, \text{mL h}^{-1}$, a substrate temperature of $T_s = 230 \, ^\circ\text{C}$, a nozzle-to-substrate distance of $d_{\text{ns}} = 20 \, \text{mm}$, and a deposition time of $t = 3 \, \text{h}$, are shown in Figure 1A–F. In these conditions, both as-prepared (amorphous) and sintered (crystalline) Pr_6O_{11} samples showed similar brain-like type microstructures (Figure 1). The average grain size was too small to be resolved by Scanning Electron Microscopy, SEM (Figure 1C,F), and was therefore determined using Transmission Electron Microscopy, TEM, and X-Ray Diffraction, XRD, analyses (see Section 2.2.). Such microstructure was found reproducible via five replicate coatings.

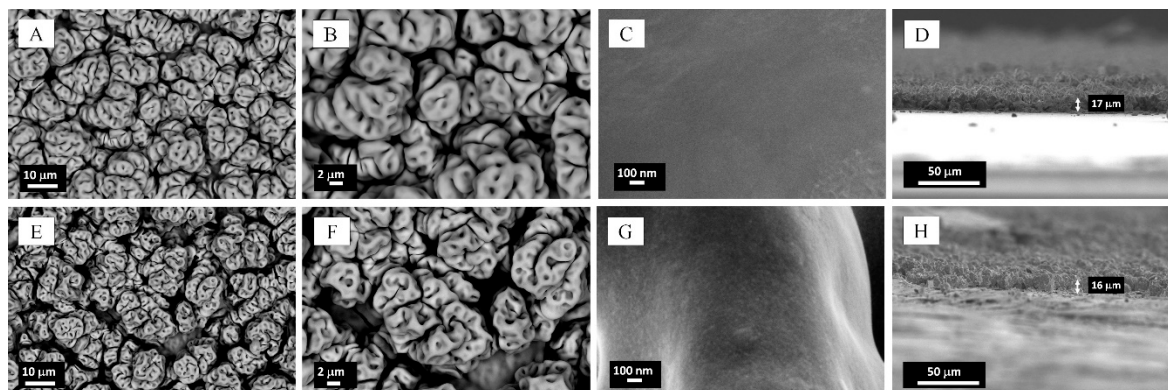


Figure 1. SEM micrographs of $\text{Pr}_6\text{O}_{11}/\text{GC}$ ESD films obtained with a $\text{EtOH}:\text{BC}$ (1:2) solution with a concentration of 0.02 M at $T_s = 230^\circ\text{C}$ for a nozzle to substrate distance of $d_{\text{ns}} = 20$ mm, a flow rate of $Q = 1.5\text{ mL h}^{-1}$, and a deposition time of $t = 3$ h. (A–C) surface view and (D) cross-section of amorphous (as-prepared) $\text{Pr}_6\text{O}_{11}/\text{GC}$; (E–G) surface view; (H) cross-section of crystalline (sintered at $T = 550^\circ\text{C}$ for 2 h in air) $\text{Pr}_6\text{O}_{11}/\text{GC}$.

With the ESD deposition technique, the microstructure of the film is controlled via the size of the droplets that impact the substrate, which depends on the solution properties (solvent density ρ , surface tension γ , boiling point $b.p.$, and electrical conductivity K) and the deposition parameters (flow rate Q , substrate temperature T , nozzle-to-substrate distance d_{ns} , and deposition time t) as per following the Gañan-Calvo's relationship (Equation (1)) [58]

$$d_{\text{droplet}} \sim \left(\frac{\varepsilon_0 \rho Q^3}{\gamma K} \right)^{1/6} \quad (1)$$

where d_{droplet} is the droplet diameter, ε_0 is the vacuum permeability and Q is the flow rate.

The physicochemical properties of the precursor solution also play a crucial role on evaporation of the solvents during the transport and spreading of the droplets when they impact the substrate, resulting in different microstructures [51,56,57]. In these ESD conditions, the boiling point of the solution of precursors, around $T = 200^\circ\text{C}$, is close to the deposition temperature (i.e., that of the substrate, $T_s = 230^\circ\text{C}$). Large droplets full of liquid are therefore expected, according to Equation (1), especially when a high flow rate of $Q = 1.5\text{ mL h}^{-1}$ is used. In addition, at a short nozzle-to-substrate distance of $d_{\text{ns}} = 20$ mm, these droplets do not have time to evaporate, and instead spread on the heated substrate upon impact. Since the drying step is occurring simultaneously with the boiling step, mechanical stress is generated by drying and contraction of the film on the heated substrate. This drives the film to severe cracks and a “brain-like” type morphology could be observed (Figure 1A,B,E,F). The average thickness of the amorphous (Figure 1D) and crystalline (Figure 1H) samples was found near similar at around $16 \pm 2\text{ }\mu\text{m}$. The mass of the samples was measured by simply weighing the RDE tips before and after deposition. The values obtained were close to the sensitivity of the scale used, so only estimates of the samples weight could be given: $0.7 \pm 0.3\text{ mg}$ was obtained for both the amorphous and crystalline samples. These values led to an apparent density of the deposits of ca. 2.23 g cm^{-3} , a value ca. three times smaller than the expected density of Pr_6O_{11} (6.55 g cm^{-3}), in agreement with the existence of macro-porosity in the thin-films (Figure 1A,B,E,F), with porosity on the smaller scale being monitored by TEM (see Section 2.2). The authors point out that an essential understanding of the brain-like type microstructure observed in Figure 1A–H would require more in-depth experimental and theoretical work, which is beyond the scope of the present contribution. The X-ray energy dispersive (X-EDS) spectra in Figure 2 confirmed the presence of Pr and O elements in both films, the amorphous one and the crystalline one, as expected. No noticeable differences in film composition were observed upon crystallization.

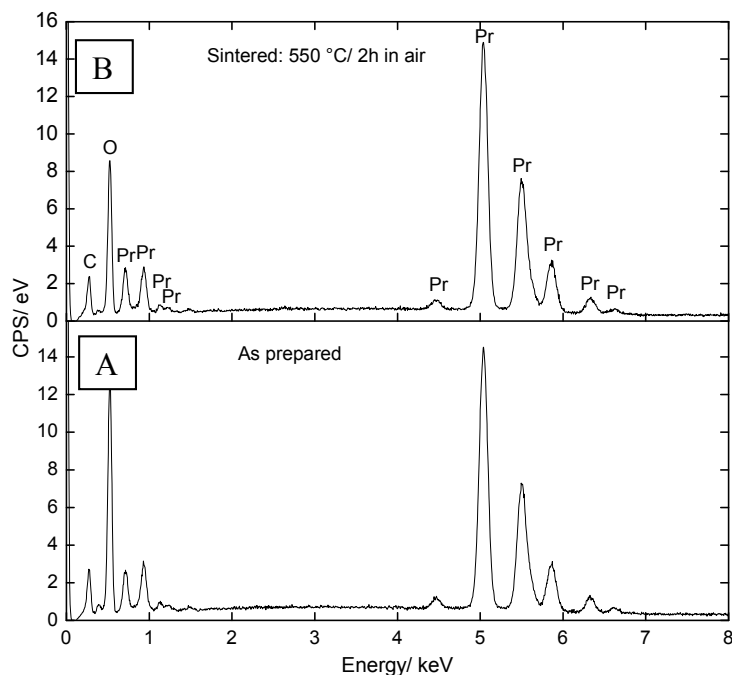


Figure 2. Typical X-EDS spectra of the Pr_6O_{11} /GC film deposited on the glassy-carbon substrate: (A) amorphous; (B) crystalline, sintered for 2 h in air at $T = 550^\circ\text{C}$.

2.2. Structural Characterization

X-ray diffraction patterns of both the as-prepared film (amorphous) and the one sintered in air for 2 h at $T = 550^\circ\text{C}$ (crystalline) are shown in Figure 3. As shown in Figure 3A, the as-prepared film was indeed amorphous, whereas all diffraction peaks of the sintered one (Figure 3B) were indexed with the fluorite cubic structure of Pr_6O_{11} (JCPDS 00-042-1121) crystallizing in the $Fm\bar{3}m$ space group ($N^\circ 225$), and of the glassy-carbon support. No secondary phases were observed within the detection limits of the powder XRD. The unit-cell parameter of the fluorite cubic structure Pr_6O_{11} was $a = 5.4678(0) \text{ \AA}$. The average crystallite size calculated by using Scherrer equation for (111), (200), (220) and (311) diffraction peaks was about 16 nm for the films sintered at $T = 550^\circ\text{C}$.

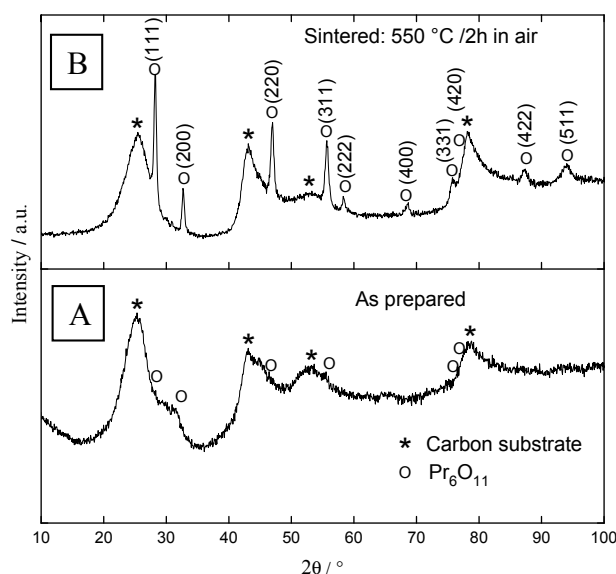


Figure 3. X-ray diffraction patterns of Pr_6O_{11} ESD film deposited on vitreous carbon substrate: (A) as-deposited (amorphous); (B) sintered for 2 h in air at $T = 550^\circ\text{C}$ (crystalline).

The microstructure was further investigated by TEM, high-resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED) as shown in Figure 4. For this, the powder was scratched from the brain-like type film sintered at $T = 550\text{ }^{\circ}\text{C}$ (crystalline). The brain-like morphology of the crystalline Pr_6O_{11} consists of numerous interconnected nanoparticles of ca. 10–20 nm on average (Figure 4A), in agreement with the XRD data. The HRTEM image in Figure 4B shows distinct lattice fringes which revealed the high crystallinity of the Pr_6O_{11} coating. In fact, the SAED pattern (Figure 4C) shows the diffraction rings for the (111), (200), (220), (311) and (222) crystal planes of fluorite cubic structure of polycrystalline Pr_6O_{11} phase, in agreement with the XRD results.

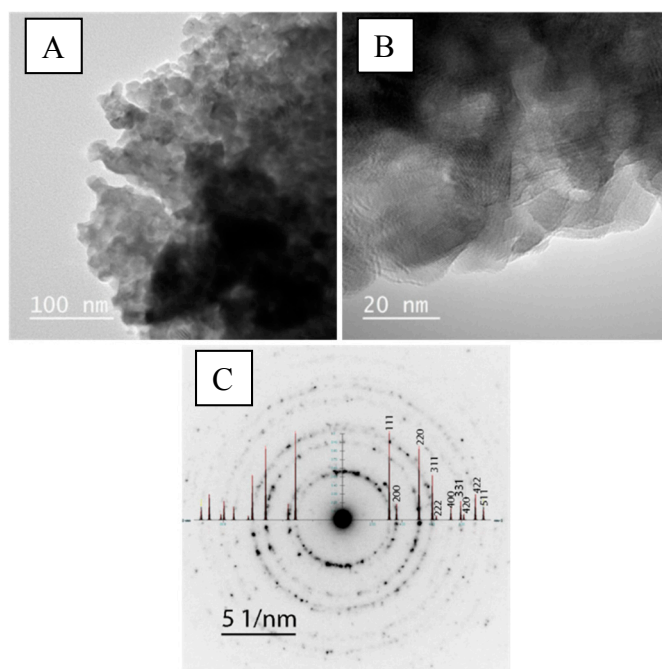


Figure 4. TEM, HRTEM, and SAED pattern of powder scratched from the brain-like type Pr_6O_{11} ESD film sintered in air for 2 h at $T = 550\text{ }^{\circ}\text{C}$ (crystalline Pr_6O_{11}): (A) TEM, (B) HRTEM, (C) SAED pattern.

2.3. Electrochemical Properties

2.3.1. Pr_6O_{11} As-Prepared (Amorphous)

The behavior of the amorphous (as-prepared) Pr_6O_{11} /GC sample (no annealing for crystallization, hereafter simply denoted *amorphous Pr_6O_{11}*) in supporting electrolyte and under inert atmosphere is presented on Figure 5 together with the voltamperograms showing incursions to low (HER) and high (OER) potential values. Obviously, the alkaline HER and OER activity of this sample was minor versus the state-of-the-art for non-noble electrocatalysts in the literature [59–64]. For this reason, focus on the ORR activity of the amorphous Pr_6O_{11} electrocatalyst will be made hereafter (Figure 6). The onset potential of the ORR is ca. $E_{\text{onset}} = 0.835\text{ V}$ vs. RHE, in line with the performances reached by Poux et al. [33,36,65] for similar types of ORR catalytic materials in absence of carbon electron-conductive additives. However, the reaction kinetics was rather sluggish, and the limiting plateau was ill-defined (Figure 6); the latter appeared at smaller current densities compared to the study of Poux et al., which can be connected to the small loading of amorphous Pr_6O_{11} electrocatalyst immobilized at the RDE tip in the present case (ca. 700 μg , see above). To be more specific, the limiting current densities monitored were far below (ca. a factor of 15) the ones expected if the ORR was complete and involving 4 electrons per O_2 molecule (in this case, the limiting current densities of ORR

should be ca. 3.1, 4.6, 6.2, and 7.7 mA cm⁻²_{geometric} at RDE revolution rates of $\Omega = 400, 900, 1600$, and 2500 rpm, respectively, these values being calculated using the Levich equation (Equation (2)):

$$j_{\text{lim}} = 0.62 n F D^{2/3} C v^{-1/6} \Omega^{1/2} \quad (2)$$

with $n = 4$, $F = 96,500 \text{ C mol}^{-1}$, $D = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [66], $C = 1.3 \text{ } \mu\text{mol cm}^{-3}$ [66] and $v = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, for a 0.1 M NaOH solution at $T = 25 \text{ } ^\circ\text{C}$.

This lower-than-expected limiting current density could be ascribed to an insufficient loading of amorphous Pr₆O₁₁ (though the authors think it is not likely given the coverage of the glassy-carbon disks being near-complete (see Figure 1)), but also to the fact that (i) the ORR predominantly proceeds according to a 2-electron pathway generating HO₂⁻ instead of OH⁻, or (ii) that the electronic conductivity of the amorphous Pr₆O₁₁ layer was insufficient to enable its complete operation (in other words, it is likely that not all the catalytic sites could operate owing to their “electrical disconnection” from the GC current collector, the effect being emphasized here because no carbon black additive was used). This will not be further investigated here, as the results of ORR on amorphous Pr₆O₁₁ were not sufficiently convincing for an application in alkaline fuel cell cathodes.

Besides, the amorphous Pr₆O₁₁ did not show adequate tolerance to NaBH₄ (Figure 7), as non-negligible NaBH₄ oxidation current was witnessed in nearly all ORR potential regions. This result is disappointing, as non-noble metals (oxides) usually show remarkable tolerance to strong reducers (fuels), e.g., rare-earth perovskites [67], monoatomic metal complexes [68–71], manganese oxides [16,69,72,73], or cobalt oxides [74].

As a result, this material does not reach sufficient performances for application in practical alkaline fuel cell systems. Therefore, the focus will be made on samples heat-treated at a sufficiently high temperature to enable crystallization of the Pr₆O₁₁ phase.

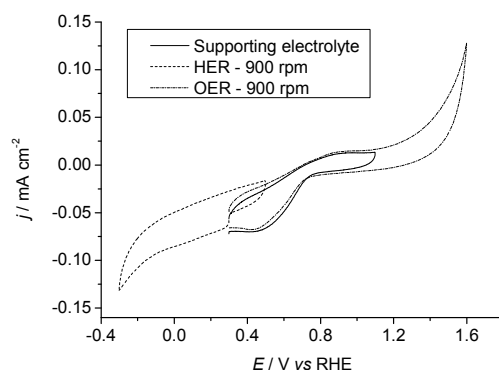


Figure 5. Voltamperogram in 0.1 M NaOH-supporting electrolyte of amorphous Pr₆O₁₁ (Ar atmosphere), with incursions in the HER and OER regions of Pr₆O₁₁; $T = 25 \pm 2 \text{ } ^\circ\text{C}$, $v = 20 \text{ mV s}^{-1}$.

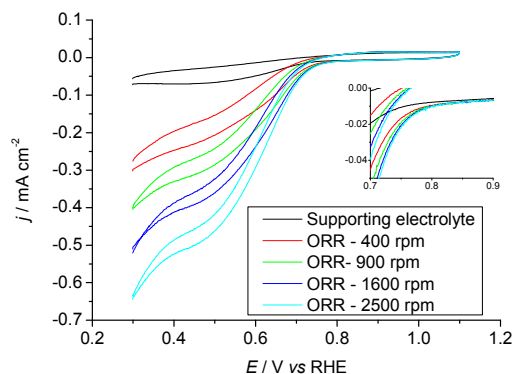


Figure 6. Oxygen reduction reaction voltamperogram in 0.1 M NaOH electrolyte of amorphous Pr₆O₁₁ (O₂ atmosphere); $T = 25 \pm 2 \text{ } ^\circ\text{C}$, $v = 5 \text{ mV s}^{-1}$.

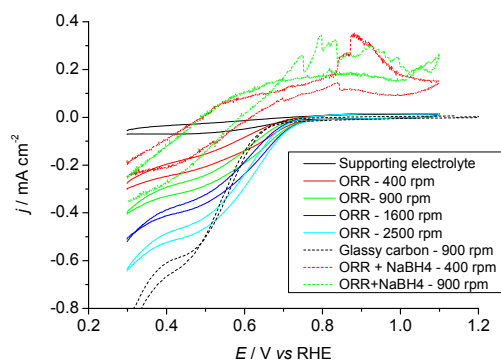


Figure 7. Oxygen reduction reaction voltamperogram in 0.1 M NaOH + 0.01 M NaBH₄ electrolyte of amorphous Pr₆O₁₁ (O₂ atmosphere); $T = 25 \pm 2^\circ\text{C}$, $v = 5\text{ mV s}^{-1}$.

2.3.2. Pr₆O₁₁ Sintered (Crystalline)

The behavior of Pr₆O₁₁ heat-treated for 2 h at $T = 550^\circ\text{C}$ (sintering/annealing that enabled crystallization of the Pr₆O₁₁ phase, see previous sections, herein denoted *crystalline Pr₆O₁₁*) in supporting electrolyte and under an inert atmosphere is presented on Figure 8. As for the as-prepared (amorphous) sample, the HER and OER activity were too small to render the material competitive versus the present state-of-the-art, even though the performances were slightly better compared to the amorphous sample. Therefore, the focus will be made on the ORR activity of the material.

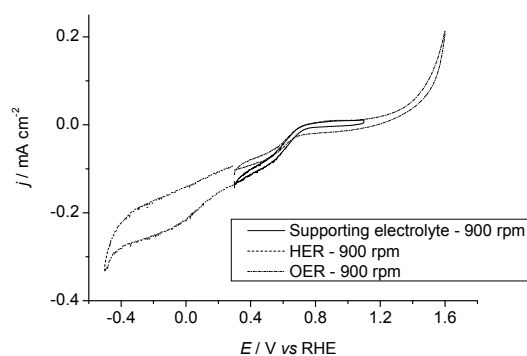


Figure 8. Voltamperogram in 0.1 M NaOH-supporting electrolyte of crystalline Pr₆O₁₁ annealed at $T = 550^\circ\text{C}$ (Ar atmosphere), with incursions in the HER and OER regions; $T = 25 \pm 2^\circ\text{C}$, $v = 20\text{ mV s}^{-1}$.

The ORR activity of the crystalline Pr₆O₁₁ sample was better than that of the as-prepared one (Figure 9A), as clearly revealed when directly superposing the two sets of data on the same axes (Figure 9B). While the onset potential value ($E_{\text{onset}} = 0.835\text{ V vs RHE}$, in the average for such class of materials [46,75–81], although in these papers, the materials were tested with carbon as electron-conductive additive) was barely changed compared to the amorphous sample, the limiting current plateaus were better defined. However, they still do not match the expected values for a 4-electron ORR, by a factor ca. 4, a behavior also noted by Poux et al. in the absence of electron-conductive additives in their inks [33,36] and by Fabbri et al. [35]. These authors linked this surprising behavior to multiple (positive) effects in the presence of carbon: (i) an enhanced electronic conductivity; (ii) a bifunctional effect between carbon (that generates HO₂[−]) and the perovskite oxide (that converts it to OH[−]); and also (iii) a ligand effect that positively modulates the electronic structure of the metal oxides. Whatever the positive influence of crystallization noted here, one can nevertheless affirm that it is still not approaching the activity of the best rare-earth oxide-based electrodes for alkaline ORR [33,36,65], and is even less than that of a state-of-the-art Pt/C electrocatalyst (Figure 9C). In addition, as was for its amorphous counterpart, the tolerance of the crystalline Pr₆O₁₁ to strong reducers was not evident, as NaBH₄ oxidation currents were monitored on the whole ORR potential range (Figure 10); this finding is in opposition to the results of Yang et al. who used a LaNi_{0.8}Co_{0.2}O₃ ORR electrocatalyst [67].

These results were reproduced for at least two different electrodes in each case: they show that crystallization of the Pr_6O_{11} phase by 2 h annealing at $T = 550^\circ\text{C}$ is beneficial to the ORR activity of the sample. The so-obtained sample, nevertheless, did not approach the performances of state-of-the-art rare-earth oxide-based ORR electrocatalysts reported in the literature [33,36,42,59,65,67], but performed in full-absence of carbon additive to enhance the electronic conduction of the electrode. Although this last property is clearly a step forward in the practical application of such materials in alkaline fuel cell cathodes, more work is needed to obtain an electrocatalyst that approaches Pt-group metal-based ORR electrocatalysts. One possibility would be that the present deposits were too thick to fully benefit from the high electronic conductivity of the glassy-carbon substrate and the outer surface of the Pr_6O_{11} sample; this shall be tested in the future for thinner (but well-covering) films at the GC substrate.

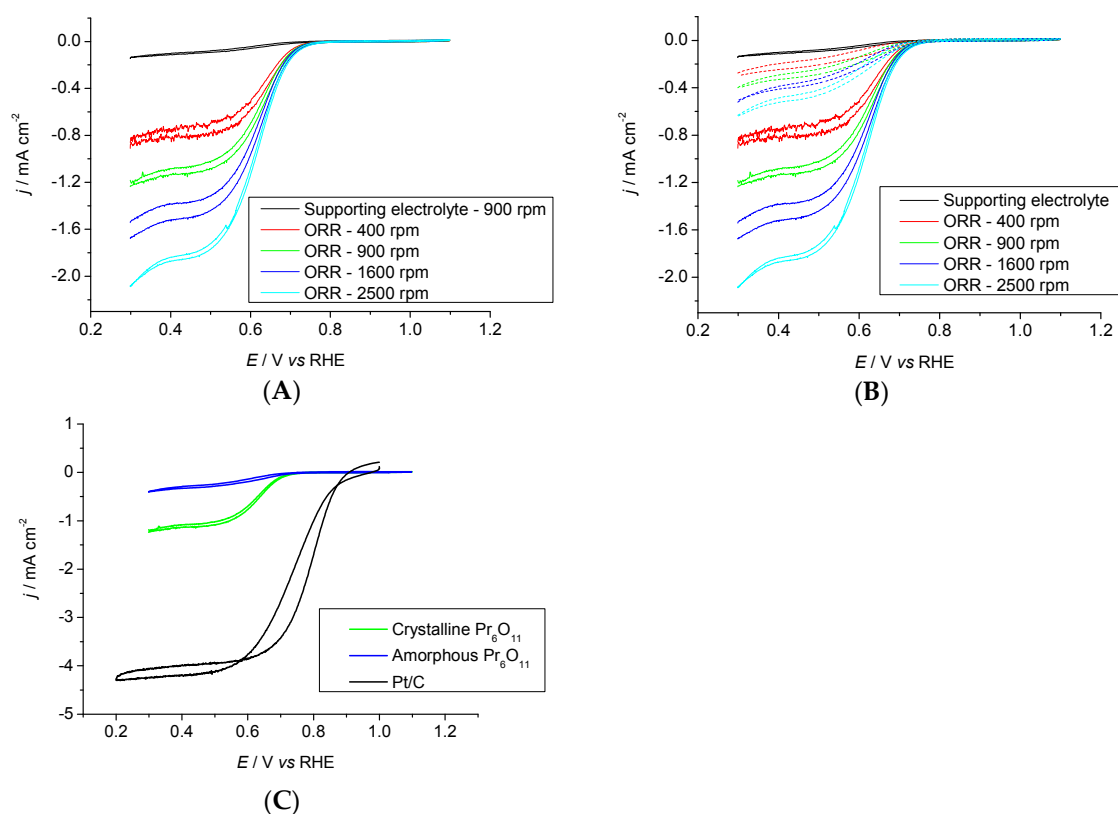


Figure 9. (A) Oxygen reduction reaction voltamperogram in 0.1 M NaOH electrolyte of crystalline Pr_6O_{11} annealed at $T = 550^\circ\text{C}$ (O_2 atmosphere), (B) comparison with amorphous Pr_6O_{11} (not-annealed, data set in dashed lines), and (C) comparison of amorphous and crystalline Pr_6O_{11} with a state-of-the-art Pt/C electrocatalyst at $\Omega = 900$ rpm; $T = 25 \pm 2^\circ\text{C}$, $v = 5 \text{ mV s}^{-1}$.

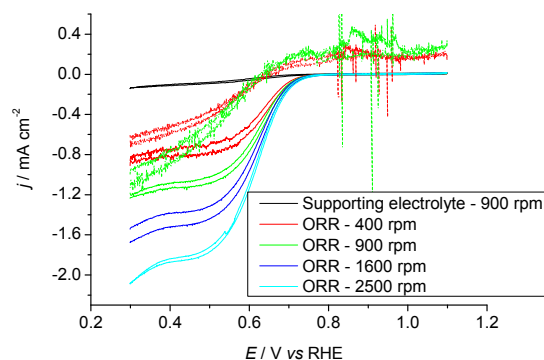


Figure 10. Oxygen reduction reaction voltamperogram in 0.1 M NaOH + 0.01 M NaBH_4 electrolyte of crystalline Pr_6O_{11} annealed at $T = 550^\circ\text{C}$ (O_2 atmosphere); $T = 25 \pm 2^\circ\text{C}$, $v = 5 \text{ mV s}^{-1}$.

3. Materials and Methods

3.1. Pr_6O_{11} Film Preparation

Pr_6O_{11} films have been deposited on glassy-carbon substrates (0.5 mm in diameter, $S_{\text{geometric}} = 0.196 \text{ cm}^2$) by Electrostatic Spray Deposition (ESD), a technique based on the principle of electrostatic atomization [51,53–57,82–86]. The ESD technique is basically a simple three-step process, as described hereafter. The first step consists of the creation of an aerosol from the precursor solution at the needle tip by applying a high dc voltage between the tip and the substrate. The second step is the transportation of the aerosol from the needle to the surface of the substrate in the electric field. The third and last step is the formation of the coating from the impact of the droplets on the heated substrate. The last two steps play a major role in the microstructure of the coating since the droplet size has to be well-controlled versus the ESD process parameters. For this, a praseodymium nitrate hexahydrate ($\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%, Aldrich) based precursor solution of 0.02 M concentration was prepared in a mixture of ethanol (EtOH , $\text{CH}_3\text{CH}_2\text{OH}$, >99.9%, VWR Chemicals, referred as EtOH) and butyl carbitol (diethylene glycol monobutyl ether $\text{CH}_3(\text{CH}_2)_3(\text{OC}_2\text{H}_4)_2\text{OH}$, Acros Organics, 99+%, referred to as BC) at an $\text{EtOH}:\text{BC}$ ratio of 1:2, under vigorous stirring. In this contribution, deposition has been carried out at a nozzle-to-substrate distance (d_{ns}), flow rate (Q), substrate temperature (T_s), and deposition time (t) of, 20 mm, 1.5 mL h^{-1} , 230°C and 3 h, respectively. During the ESD, the voltage was fixed to approximately 5–7 kV. The as-prepared films (noted $\text{Pr}_6\text{O}_{11}/\text{GC}$) were found to be amorphous and a subsequent sintering at $T = 550^\circ\text{C}$ in air for 2 h led to the crystallization of the films. The area of the deposited Pr_6O_{11} was 0.196 cm^2 , corresponding to a full-coverage of the glassy-carbon tip of the rotating disk electrode (RDE). It is worth adding that the $\text{Pr}_6\text{O}_{11}/\text{GC}$ films prepared herein did not contain electron-conductive additives (e.g., carbon black), which is often encountered in the literature and known to modulate the apparent activity of such rare-earth-based samples [32–36].

3.2. Microstructural and Electrochemical Characterization

X-ray diffraction (XRD, Philips X'Pert-MPD system, $\text{Cu K}\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$) in the Bragg–Brentano configuration was used to determine the crystal structure and purity of the prepared films. Phase identification was carried out using the International Centre for Diffraction Data (ICDD), the lattice parameters being determined from the refined X-ray pattern by profile matching using the Fullprof software [87]. The surface-morphology of each film was analyzed by scanning electron microscopy (ZEISS Ultra 55 instrument, Jena, Germany) with a field emission gun (FEG) and X-ray energy-dispersive spectroscopy (XEDS) for composition analysis. High-resolution transmission electron microscopy (HRTEM) and selective area electron diffraction (SAED) were also performed on a JEOL 2010 (JEOL, Tokyo, Japan) equipped with a LaB_6 filament to evaluate the particle size and crystal structure. For the TEM analysis, the samples were prepared by scratching the surface of amorphous or crystalline Pr_6O_{11} using the diamond tip, and immobilizing the scratched Pr_6O_{11} on a copper (Cu) holey carbon grid.

Electrochemical measurements of the activity of both amorphous and crystalline Pr_6O_{11} electrodes were performed towards usual reactions of electrocatalysis (namely the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and the oxygen reduction reaction (ORR), the latter one performed in absence or presence of a strong reducer in solution (NaBH_4) for potential application in direct borohydride fuel cell cathodes [16,72,88–90]). They were performed in a Pyrex®-based four-electrode cell, with glassy-carbon as the counter electrode (to avoid any possible contamination of the working electrode (WE) with the dissolution of the, usually Pt-based, counter electrode [91], a very likely occurrence in base electrolytes [92–95]), Pt as the auxiliary electrode, a hydrogen reference electrode (all the potential values are expressed on the RHE scale hereafter) and $\text{Pr}_6\text{O}_{11}/\text{GC}$ (either bare (amorphous) or heat-treated (crystalline)) as the WE. The cell is equipped with an internal PTFE beaker to limit contamination by the possible dissolution of the Pyrex in strong base [96]. The potentiostat used was a multichannel VMP3 from Bio-Logic® piloted by the EC-lab software. In any case, the cell

and glassware were soaked in Caro's acid overnight and thoroughly rinsed using ultrapure water (18.2 MΩ cm, <3 ppb total organic carbon, Millipore[®], Billerica, MA, USA) prior to each measurement. All the electrochemical experiments were performed using a dynamic correction of the Ohmic-drop, the high-frequency resistance being measured prior to each experiment at 10,000 Hz and automatically corrected at 85%.

An aqueous solution of 0.1 M NaOH at $T = 25 \pm 2$ °C for ORR, OER, and HER study, and aqueous solution of 0.1 M NaOH + 10^{-2} M NaBH₄ aqueous solution ($T = 25 \pm 2$ °C) for borohydride oxidation reaction (BOR) and ORR in the presence of BH₄[−] for tolerance study, have been used. The aqueous solutions were saturated by bubbling Ar or O₂ in solution (4N purity, Messer, Bad Soden, Germany), depending on the test. All the salts used to prepare the electrolytes were purchased in Suprapur[®] quality (Merck, Darmstadt, Germany) and used without further purification. The electrolytes were prepared using ultrapure water.

4. Conclusions

In this work, we have successfully prepared brain-like type hierarchical nanostructured Pr₆O₁₁ by electrostatic spray deposition (ESD) on glassy-carbon tips of rotating disk electrodes (RDE). These materials have been tested in liquid alkaline electrolyte (0.1 M NaOH) in view of their potential application in alkaline electrolyzers or alkaline fuel cells. The as-prepared Pr₆O₁₁ film is amorphous and shows minimal HER, OER, and ORR activities in 0.1 M NaOH electrolyte. The amorphous nature of the film disappears upon 2 h sintering in air at $T = 550$ °C, leading to crystalline *Fm* $\bar{3}$ *m* fluorite cubic structure. In that case, the brain-like type microstructure consists of agglomerated crystalline nanoparticles, with sizes in the range of ca. 10–20 nm on average. The crystalline Pr₆O₁₁ exhibits better ORR activity than its amorphous counterpart but still fails to direct the reaction towards a complete 4-electron pathway and to reach the activity of the best non-PGM electrocatalysts reported in the literature (and even less than that of PGM-based electrocatalysts). In addition, the material does not exhibit significant HER and OER activities and does not seem tolerant to BH₄[−] fuel. Nevertheless, the significant ORR performances reached were obtained in the absence of any electron-conductive additive, which grants the material some interest for potential use in alkaline fuel cell cathodes and leaves hope for improvements in activity if the electronic conductivity of the oxide layer is improved and/or if its thickness is decreased.

Author Contributions: R.S. performed the materials syntheses, some of their materials' characterizations, some of the data analysis, and participated in the writing. V.M. performed some of the materials' characterizations. M.C. performed the electrochemical analyses and made the corresponding data analysis. E.D. and M.C. equally performed some of the materials' characterizations, some of the data analysis, and participated in the writing of the contribution.

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