Nanostructured Gas Diffusion Layer to Improve Direct Oxygen Reduction Reaction in Air-Cathode Single-Chamber Microbial Fuel Cells

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Article

Nanostructured Gas Diffusion Layer to Improve Direct Oxygen Reduction Reaction in Air-Cathode Single-Chamber Microbial Fuel Cells

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Abstract: The aim of this work is the development of new nanostructured-gas-diffusion-layer (GDL) to improve the overall behaviour of Air-Cathode Single-Chamber-Microbial-Fuel-Cells (SCMFCs). The design of new nanostructured-GDL allowed exploiting all nanofibers 'intrinsic properties, such as high surface ratio to volume, high porosity, achieving a good oxygen diffusion into the proximity of catalyst layer, favouring thus the direct oxygen-reduction-reaction (ORR). Nanostructured-GDLs were prepared by electrospinning process, using layer-by-layer deposition to collect 2 nanofibers' mats. The first layer was made of cellulose nanofibers able to promote oxygen diffusion into SCMFC. The second layer, placed outwards, was based on polyvinyl-fluoride (PVDF) nanofibers to prevent the electrolyte leakage. This nanostructured-GDL plays a pivotal role to improve the overall performance of Air-Cathode-SCMFCs. A maximum current density of (132.2 ± 10.8) mA m-2 was obtained, which is two times higher than the one reached with commercial-PTFE (58.5 ± 2.4 mA m-2), used as reference material. All results were analyzed in terms of energy recovery parameter, defined as ratio of generated power integral and the internal volume of devices, evaluating the overall SCMFC performance. SCMFCs with a nanostructured-GDL showed an energy recovery one order of magnitude higher than the one obtained with commercial-PTFE.

Keywords: nanostructured gas diffusion layer; electrospinning; triple phase boundary; oxygen reduction reaction; microbial fuel cell

1. Introduction

In the scenario of transition from carbon-based economies towards sustainable human developments, all technologies based onto renewable energy sources are becoming emerging systems [1]. Among all possible renewable energy sources, like wind, solar, hydro-and geo-thermal and biomass, microbial fuel cells (MFCs) have gained great interest in recent years since these bio-electrochemical devices are able to combine the power production with some processes like water treatments [2,3], bioremediation [4], and sensing [5–7], obtained by involving a particular class of bacteria into MFCs, known as electroactive bacteria [8–12]. These microorganisms are involved as biocatalysts into the anode compartments, thanks to their effective role to oxidize anaerobically the organic matter dissolved into electrolyte and to release the produced electrons from themselves to anode electrode. Therefore, electroactive bacteria can direct transduce the chemical energy, entrapped into organic matter, into electrical energy [10–12]. Released electrons continuously flows to cathode compartment through an external load, ensuring their re-combination with terminal electron acceptors (TEAs).

In an opened air configuration, common TEA is the oxygen, achieving thus the direct oxygen reduction reaction onto the cathode electrode, avoiding as much as possible the intermediate one that

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occurred hydrogen peroxide's (H2O2) production, revealed toxic for microorganisms. As deeply demonstrated and confirmed by several works in the literature [13–17], oxygen reduction reaction at the cathode was commonly involved, since the selection of oxygen as TEAs results to be pivotal to guarantee the best compromise/balance among the MFCs' usage for power production and for applications directly in the environment. Moreover, the presence of platinum as the best-performing catalyst towards direct-ORR allowed overcoming all limitations addicted to the slow kinetics of this reduction reactions [13–17]. A key component that strictly affect the overall devices' performance is Gas Diffusion Layer (GDL), which resulted to be accountable for diffusion of reactant gases, such as oxygen, removal of exceeded water in proximity of catalyst layer and the minimizing as more as possible the electrolyte leakage [18]. The ideal GDLs must satisfy several properties, such as high gas diffusion [19,20], good bending stiffness, continuous porosity, air permeability, water vapor diffusion, high surface area to volume ratio to ensure the water removal, good electrical and electronic conductivity to ensure the proper electrons' transfer and suitable mechanical stability [18]. All satisfied properties would allow to ensure the optimization of triple contact zone, which is defined as the zone in proximity of which protons, electrons, and oxygen' molecules must flow to properly recombine one with each other, leading thus to ensure the direct oxygen reduction reaction [21–24]. For what concerning air-cathode single chamber microbial fuel cells (SCMFCs), commonly the GDL is carbon-based materials placed between the air and the catalyst layer [25]. On its outer side, a hydrophobic coating, typically based on polytetrafluoroethylene (PTFE), was applied leading thus to remove the excess of water, also preventing the cathode flooding [26–30]. Guerrini et al. [30] demonstrated the effective influence of PTFE, involved into GDL in an open-air cathode MFCs, onto the overall performance. They observed that a high content of PTFE in the cathode electrode played a detrimental role as inhibitor for ORR catalysis, improving the flooding level in the catalyst layer, limiting thus the MFC productivity. Moreover, many works in the literature, in the main fields of fuel cell technology, focused their attention on the GDLs' structure, that could be a bottleneck for improving of functionality of this layer [18–30]. Indeed, during last decades, nanostructured materials, involved to design GDLs, have gained a great interest to achieve the promising functionality in terms of surface morphology to ensure a proper reactant gas diffusion, a suitable water removal and a structural refinement [18,31,32].

To overcome all limitations addicted to the amount of PTFE, which can induce an incomplete wetting of the cathode electrode, to its high cost and to its toxicity, and with the main purpose to achieve the best compromise between the hydrophobicity, responsible for water expelling, and hydrophilicity, effective for water retaining, in the present works a new nanostructured GDL was proposed. Furthermore, the main goal of the present work is the development of a new nanostructured-gas-diffusion-layer (GDL) to improve the overall behaviour of Air-Cathode Single-Chamber-Microbial-Fuel-Cells (SCMFCs), leading thus to obtain the best compromise among hydrophobic and hydrophilic properties of GDL. Nanostructured-GDLs were prepared by electrospinning process, using a layer-by-layer deposition to collect 2 different nanofibers' mats, avoiding the needed of a binder to reduce the contact between 2 nanostructured layers and carbon backbone (Carbon paper, CP). The first layer was made of cellulose nanofibers that play a crucial role to promote oxygen diffusion into SCMFC, also ensure the correct hydrophilicity and improve the water retention in proximity of catalytic active sites, avoiding the decrease of proton conductivity of the electrolyte by dehydration [29,30]. The second layer, placed outwards, was based on polyvinyl-fluoride (PVDF) nanofibers with the main purpose to prevent the electrolyte leakage, while allowing oxygen free to flow and the correct water removal from cathode electrode.

The design of new nanostructured-GDL allowed exploiting all nanofibers 'intrinsic properties, such as high surface ratio to volume, high continuous porosity, and light weight, achieving thus a good oxygen diffusion into the proximity of catalyst layer, ensuring, and favouring the direct oxygen reduction reaction (ORR) and at the same time preventing the water flooding in correspondence of catalyst layer. In the present work, the catalyst layer is based onto Platinum, which is considered as the ideal catalyst layer, able to provide a number of electrons as much as possible close to 4, guaranteeing the direct-ORR [35]. Both of two nanostructured layers were directly collected onto

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carbon paper. Onto the inner side of carbon paper electrode, a catalyst layer made of Pt/C was applied to ensure the direct ORR. To demonstrate how nanostructured GDL can improve the overall performance of Air-Cathode-SCMFCs, this cathode electrode was applied into the devices and compared with the one that presents a commericial-PTFE, made of polytetrafluoroethylene (PTFE). A maximum current density of (132.2 ± 10.8) mA m-2 was obtained, which is higher than the one reached with commercial-PTFE, equal to (58.5 ± 2.4) mA m-2. All reached results were analysed in terms of the energy recovery parameter, defined as the ratio of the generated power integral and the internal volume of the devices, evaluating the overall SCMFC performance, as already reported in our previous work [36]. SCMFCs with a nanostructured-GDL showed an energy recovery equal to 60.83 mJ m-3, which was one order of magnitude higher than the one obtained with commercial-PTFE, close to 3.92 mJ m-3. All these latter results open the doors to design the entire nanostructured cathode electrode in SCMFCs. The nanostructured cathode electrode may be done by carbon nanofibers doped with nitrogen (N-CNFs), which play a pivotal role as promising catalyst layer for direct ORR as demonstrated in our previous work [11] and can be employed as a carbon backbone to ensure the electron transfer produced and released by microorganisms into the anode compartment.

2. Materials and Methods

2.1. Gas Diffusion Layer package and nanofibers synthesis

The layer-by layer deposition is ensured by implementing the electrospinning process (NANON 01A electrospinning apparatus MECC, LTD). One of the great advantages of this technology, indeed, consists into ability to connect two different nanofibers' layers without the using of binder, required to ensure the connection between dried nanofiber mats and CP material. In particular, two different layers were obtained: i) the first layer is made of cellulose nanofibers, obtained by a starting polymeric solution based on cellulose acetate (Mw=, Sigma Aldrich) dissolved into N-N DMF (assay 99.8%, Sigma Aldrich); ii) the second layer, on the contrary, is composed by 2g of polyvinyl fluoride (PVDF, Mw=150 kDa, Sigma Aldrich) dissolved into a mixture of N-N DMF and acetone with a volume ratio of 1:1. During the electrospinning process, the working voltage between the needle and planar counter electrode is fixed at 26 kV with a flow rate of 0.5 mL h-1. The working distance between the needle and substate is equal to 15 cm. After the deposition of first layer made of cellulose acetate nanofibers (CA nanofibers), the whole mat must be properly hydrolyzed with the main purpose to obtain a final mat of cellulose nanofibers able to ensure the adequate hydrophilicity to improve not only the oxygen diffusion but, at the same time, a proper water removal. As fabricated-CA nanofibers were hydrolyzed in 0.05 mol L-1 NaOH/ethanol (purchased from Sigma Aldrich) solution for 24 h at room temperature, followed by thoroughly washing with double-distilled water until the supernatant reached neutral. Subsequently, the deposition of PVDF nanofibers is achieved to ensure the correct balance between hydrophilic properties and hydrophobic features, preventing possible leakage of electrolyte solution.

2.2. SCMFCs architecture and operation

As deeply used in our previous work [10,11], a squared shape open-air cathode SCMFCs is used during the whole experiment. The devices,realized by 3D printer (OBJET 30] are membrane-less cells with electrolyte in common between anode and cathode. The distance between anode and cathode compartments was ensured by an intermediate compartment. The total internal volume is equal to 12.5 mL and both anode and cathode electrodes show a geometric surface area close to 5.76 cm2. Both anode and cathode electrodes were carbon-based materials, carbon paper (CP, purchased from Fuel Cell Earth, USA).. In the present work, all anode electrodes have been obtained from previous experiments, conducted in our laboratories [36]. Therefore, on anode surfaces mixed electroactive bacteria were growth, acting as microbic biofilm. For what concern cathode electrodes, on the inner side of cathode electrode, a common catalyst layer based on platinum (0.5mg cm-2 of Pt/C obtained by Sigma Aldrich) and 5wt% of Nafion (Sigma Aldrich) was applied [34]. On the outer side of cathode electrode, with the main purpose to improve the triple contact zone, leading thus to ensure the direct

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ORR and consequently increase the overall devices' performance, two different GDLs were proposed and compared: i) the first one is made of a nanostructured GDL, as explained in the previous paragraph; ii) the second one is a commercial-PTFE, composed by Polytetrafluoroethylene (PTFE) layer. The electrolyte is a water-based solution containing 12mM of sodium acetate, used as carbon-energy source, and other compounds (5.8 mM of ammonium chloride and phosphate buffer saline solution (PBS) [10–12]) suitable for the preservation of metabolic activity of microorganisms. Titanium wires were used to ensure a good electrical contact and, anode and cathode were connected with a multichannel data acquisition unit (Agilent 34972 A). To evaluate the overall SCMFCs' performance, an external load of 1kΩ was applied. Moreover, during the whole experiments, a fed bath mode is implemented to substitute the old electrolyte with the new one. According to this method, the replacement of electrolyte is carried out when voltage reaches values close to 0V. All the experiments were conducted in duplicate.

2.3. Characterizations and measurements

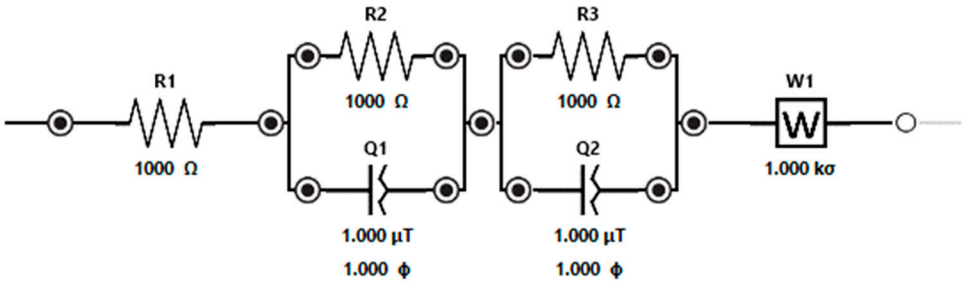
Field Emission Scanning Electron Microscopy (FESEM, Supra operating from 5 kV to 10 kV), is used to evaluate the morphological properties of nanostructured gas diffusion layer (GDL). With the main purpose to confirm the effective role of high continuous porosity, also inducing an increased surface area to volume, onto diffusion of oxygen species inside the devices and onto the balance between water retaining and removing, FESEM images were analysed with an imaging software (ImageJ).

Final porosity of both samples, nanostructured-GDL and commercial-PTFE, were indirectly determined by dividing the volume occupied by nanofiber (V_{NF}) or PTFE layer (V_{PTFE}), respectively, by total volume (V_{tot}).

$$\phi = \frac{(V_{NF} \text{ or } V_{PTFE})}{V_{TOT}}, \quad (1)$$

To evaluate how nanostructured-GDL can affect SCMFCs performance, polarization curves are defined through Linear Sweep Voltammetry (LSV) performed by using Palmsens potentiostat (Palmsens4, Netherlands)). LSV characterizations were performed at the end of experimental study. Moreover, in the present work LSV characterization is provided by implementing a voltage range from open circuit to a short circuit with a rate of 0.1 mV s-1. The electrocatalytic properties of all diverse cathodes were assessed through electrochemical impedance spectroscopy (EIS), employing a Palmsens potentiostat. For EIS, the sinusoidal signal had an amplitude of 25 mV and the frequency was spanned between 150 kHz and 200 mHz. During EIS characterization, the fixed resistor method was employed, by applying an external resistor of 100 Ω [12].

All experimental data were fitted by defining the equivalent circuit, as reported in Scheme 1, to quantitatively evaluate the electrical parameters: i) R1 represents the series resistance, accounting for electrolyte and wiring resistances; ii) R2 and R3 denote the charge transport inside the electrode and the charge transfer at the electrode/electrolyte interface resistances, respectively. Due to porous nature of cathode electrodes, constant phase elements, Q1 and Q2 are used to model the corresponding double layer capacitances [12].; and finally, iii) Warburg element was included to model low frequency feature, commonly corresponding to the species diffusion.



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Scheme 1. Equivalent circuit used to fit the impedance spectra.

3. Results and Discussion

3.1. Morphological properties of nanostructured-GDL and commercial-PTFE

The morphological properties of nanostructured-GDL were reported in **Figure 1a)**, highlighting thus the pore distribution in these samples. Indeed nanostructured-GDL are characterized by pores with dimensions in the range of few micrometers, leading thus to exhibit a higher surface area to volume ratio than the one obtained with commercial gas diffusion layers, commercial-PTFE (see Figure 1b). ImageJ software was used to define the surface area of these samples and to indirectly determine the porosity distribution of all samples, by applying Equation 1. Figure 1c) allowed confirming that the porosity distribution of nanostructured GDL, close to 77%, results to be higher than the one when commercial-PTFE was applied (equal to 25%).

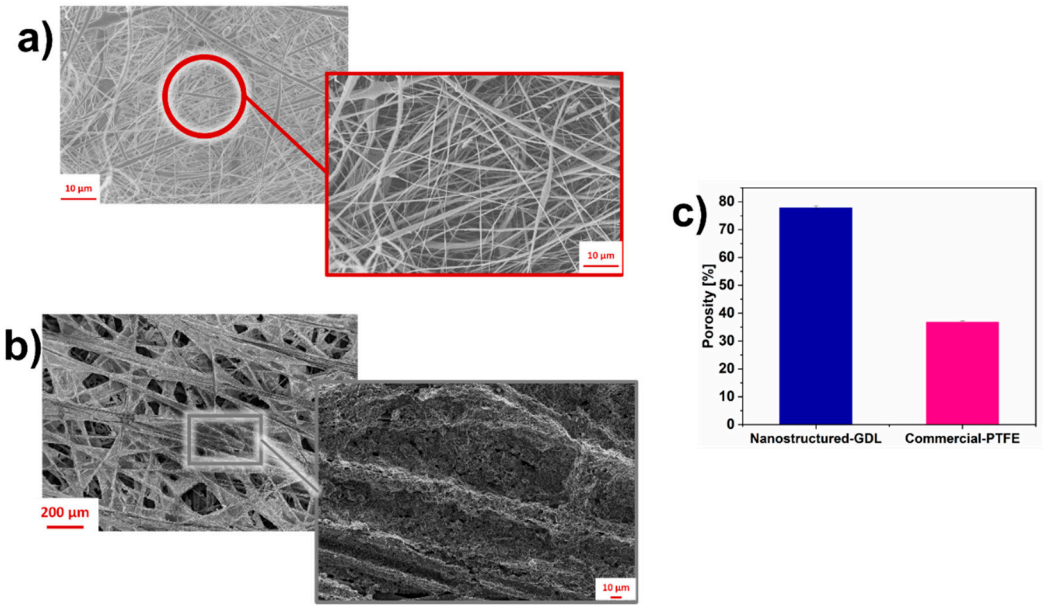

Figure 1. a) Morphological properties of nanostructured-GDL, confirming high porosity of samples, as highlighted from higher magnification, underlined by red box; b) Morphological properties of commercial-PTFE applied onto carbon paper CP; c) Evaluation of porosity distribution of nanostructured-GDL compared with the one reached with commercial-PTFE.

These intrinsic properties of nanofibers with particular attention on their high continuous porosity can play a pivotal role into the enhancement of oxygen diffusion in proximity of triple contact zone, ensuring thus a better oxygen transport in proximity of catalytic active sites.

3.2. SCMFCs performance

As previously described, at the beginning of experiments, anodes were obtained by preceding experiments [36], leading thus to employ a biofilm formation onto all anode surfaces. For all cathode electrodes, a catalyst layer based on platinum is applied, while nanostructured-GDL and commercial-PTFE were compared, to evaluate how can affect the overall performance of SCMFCs. **Figure 2** represents the current density trends over time. Nanostructured-GDL reached a maximum current density equal to (132.2 ± 10.8) mA m-2, which is double of the one reached with commercial-PTFE (maximum current density close to (58.5± 2.4) mA m-2), used as reference material. Since the anodic compartments of both kinds of devices are nominally identical, the differing performance of the SCMFCs can be directly attributed to the use of diverse GDLs applied onto cathode electrodes.

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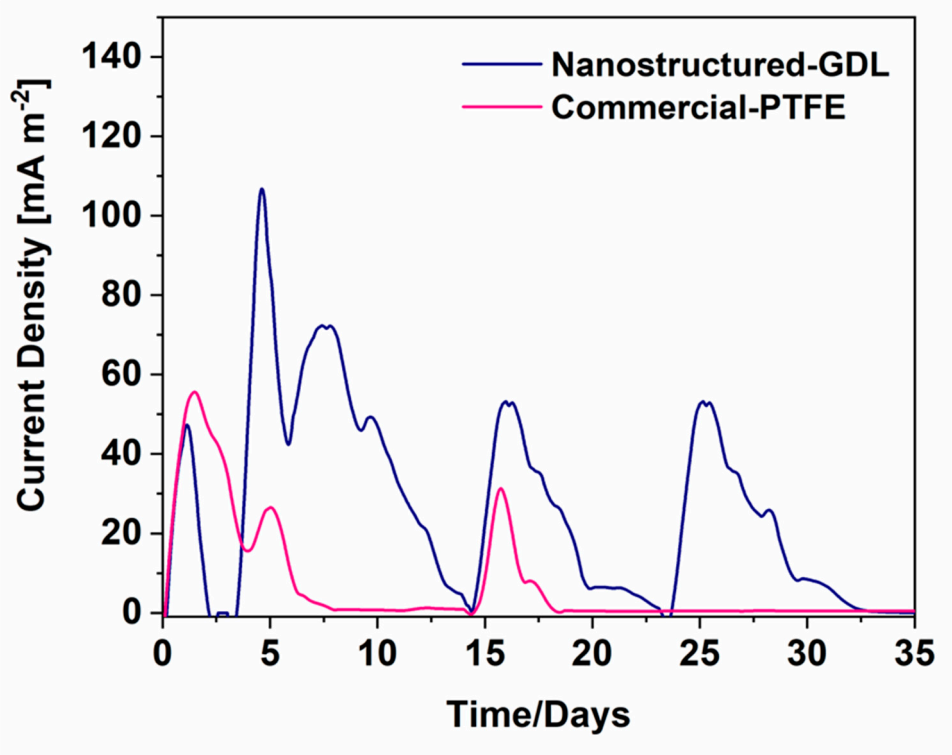

Figure 2. Comparison of average current density trend of SCMFCs with nanostructured-GDL and current density trend reached by SCMFCs with commercial-PTFE, defined as reference cathode electrode.

This latter result allowed confirming the key role of nanostructured-GDL. Indeed, nanostructured-GDL was able to improve the triple contact zone, also guaranteeing a better oxygen diffusion in proximity of catalytic active sites and, at the same time, thanks to the presence of hydrophilic cellulose-NFs layers, it ensures the exceed water removal from catalytic sites. The combination of these features affects the electrocatalytic efficiency of electrode toward direct-ORR, reflecting thus onto the augmented overall SCMFCs' performance.

All considerations were confirmed by polarization curves (LSV) analysis, represented in **Figure 3a),** and by electrochemical characterizations, represented in terms of Nyquist plot in **Figure 3b).**

Figure 3a) reported all LSV curves, related to both GDLs, granting to evaluate how maximum power density with nanostructured-GDL was up to the double of the ones reached by SCMFCs with commercial-PTFE, defined as control device for the whole experiment.

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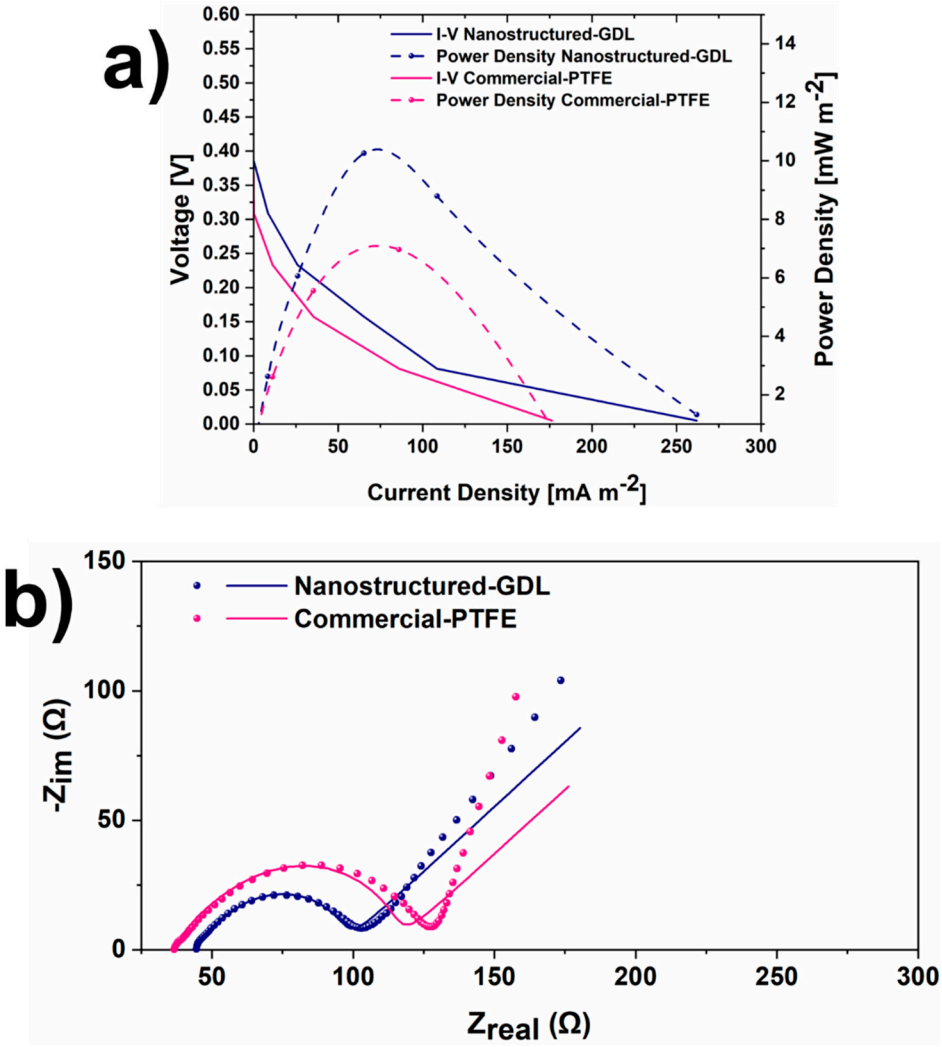

Figure 3. a) Polarization curves obtained by LSV characterization. Potential vs. current density curves (left axis, straight lines) and power density vs. current density (right axis, dash lines) curves of SCMFCs with nanostructured-GDL and commercial-PTFE, used as reference. b) Typical impedance spectra of nanostructured-GDL (blue dot and line) and commercial-PTFE (pink dot and line).

Both of SCMFCs devices reach a similar open circuit voltage (OCV) close to 0.4V, while SCMFCs with nanostructured-GDL achieved a higher short circuit current (close to 262±5 mA m-2) that the one obtained with commercial-PTFE (176.4±3.2 mA m-2). Since nanostructured-GDL can affect and favor the direct ORR, ensuring the best oxygen diffusion into SCMFCs, the variation of total cathodic resistance over time was investigated through EIS. Typical Nyquist plots are represented in **Figure 3b),** comparing nanostructured-GDL and commercial one. The curves obtained by fitting procedure are overlaid on the experimental data (**see Figure3b**). **Table 1**, on the contrary, summarized all resistance values.

Table 1. Typical resistance values (R1, R2 and R3) calculated from the fitting procedure on Electrochemical Impedance Spectroscopy (EIS) data. For each parameter, the maximum variation observed between three nominally identical Microbial Fuel Cells (MFCs) was 10%.

Cathode electrodes	R1 [Ω]	R2 [Ω]	R3 [Ω
Nanostructured-GDL	44.3	12.04	38.4
Commercial-PTFE	36.9	25.7	50.5

As highlighted in Figure 3b), all SCMFCs show a similar value of series resistance R_1, independently of cathode electrodes. This is to be expected, since electrolyte, wires and electrical connection are identical for all SCMFCs. Moreover, the lower is the charge transfer at the electrode/electrolyte interface R_3, higher is the capacity of cathode electrode to ensure a faster electrons flow. This result demonstrates the effectiveness of nanostructured-GDL to ensure an enhancement of oxygen diffusion, improving consequently the occurring of direct-ORR and the overall SCMFCs performance. A similar trend is observed for the transport resistance R_2, which is visible in the high-frequency smaller arc sketched in Figure 3b).

A lower R_2 defines an increasing of electrode transport properties and since all other aspects of cathode electrodes are the same, it is possible to confirm how nanostructured-GDL results to be more efficient in carrying out ORR.

Moreover, in line with all obtained results, the analysis performed in terms of energy recovery parameter, defined as ratio of generated power integral and the internal volume of devices, allow evaluating the overall SCMFC performance. SCMFCs with a nanostructured-GDL showed an energy recovery equal to 60.83 mJ m-3, which was one order of magnitude higher than the one obtained with commercial-PTFE, close to 3.92 mJ m-3

4. Conclusion

In the present work, nanostructured-GDL was designed as new gas diffusion layer to improve the oxygen diffusion inside SCMFCs, exploiting the intrinsic properties of nanofibers, such as high porosity, high surface area to volume ratio and light weight. Moreover, through electrospinning process, a direct deposition of nanofiber mats can be collected onto carbon-based materials, used as cathode electrodes, without the necessity of binder to bond GDL with the carbon backbone. Morphological properties confirm a higher porosity obtained with nanostructured-GDL, than the one reached when commercial-PTFE is applied as reference results.

Moreover, all obtained results demonstrate that nanostructured-GDL play a pivotal role to improve all SCMFCs performance. Indeed, SCMFCs with nanostructured-GDL reach a maximum current density which is double of the value achieved when commercial-PTFE is analyzed. Since all other aspects are in common between all cathode electrodes, it is possible to confirm that all difference can be addicted to the presence of nanofiber mats as GDL. All obtained results demonstrate the effectiveness of nanostructured-GDL to ensure an enhancement of oxygen diffusion, improving consequently the occurring of direct-ORR and the overall SCMFCs performance.

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