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Nanofiber-based gas diffusion layer for improve performance in Air-Cathode Microbial Fuel Cells

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Abstract:

This work investigates a new nanostructured gas-diffusion-layer (nano-GDL) to improve perfor-10 mance of air-cathode Single-Chamber-Microbial-Fuel-Cells (a-SCMFCs). The new nano-GDLs im-11 proves the direct oxygen-reduction-reaction by exploiting the best of nanofibers from electrospin-12 ning in terms of high surface ratio to volume and high porosity, and laser-based processing to pro-13 mote adhesion. Nano-GDLs by electrospinning were fabricated directly collecting two nanofibers 14 mats on the same carbon-based electrode, acting as the substrate. Each layer was designed with a 15 specific function: water resistant, oxygen permeable polyvinylidene-difluoride (PVDF) nanofibers 16 served as a barrier to prevent water-based electrolyte leakage, while an inner layer of cellulose nan-17 ofibers was added to promote oxygen diffusion towards the catalytic sites. The maximum current 18 density obtained for a-SCMFCs with the new nano-GDLs is (132.2 ± 10.8) mA m⁻², and it doubles the 19 current density obtained with standard PTFE-based GDL (58.5 \pm 2.4 mA m⁻²), used as reference ma-20 terial. The energy recovery (EF) factor, i.e. the ratio of the power output to the inner volume of the 21 device, was then used to evaluate the overall performance of a-SCMFCs. a-SCMFCs with nano-GDL 22 provided an EF value of 60.83 mJ m⁻³: one order of magnitude higher than the value of 3.92 mJ m⁻³ 23 obtained with standard GDL. 24

Keywords: Electrospinning; Fuel Cell; Laser-induced nanomaterials; Microbial Fuel Cells; Gas Diffusion Layer;; Triple phase boundary; Oxygen Reduction Reaction.

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1. Introduction

The transition from carbon-based economies to sustainable human development, is 30 boosting renewable energy systems [1]. Alongside the more traditional technologies for 31 the valorization of renewable energy, like wind, solar, hydro-and geo-thermal and bio-32 mass, microbial fuel cells (MFCs) have gained great interest in recent years. MFCs are 33 bio-electrochemical devices that combine a power production mechanism similar to that 34 of traditional fuel cells, with biotechnological processes like water treatment [2-3], biore-35 mediation [4], and sensing [5-7], thanks to the presence of electroactive bacteria at their 36 anodes [8-12]. These microorganisms can directly transduce the chemical energy, en-37 trapped into organic matter, into electrical energy. Indeed, electroactive bacteria work as 38 anodic biocatalysts in anaerobic conditions, oxidizing organic matter dissolved into the 39 electrolyte and releasing the produced electrons to the anode. Electrons flow continu-40 ously to the cathode compartment where their re-combination with terminal electron 41 acceptors (TEAs) is ensured. MFCs in open-air configuration use oxygen as the TEA. 42

The target cathodic reaction is the direct oxygen reduction reaction (ORR). As demon-43 strated by several works in the literature [13-17], ORR is the usual choice for the cathodic 44 reaction as oxygen maximizes power production while allowing environmental applica-45 tion of MFCs. Catalysts are needed to promote the ORR according to the direct reduction 46 of O₂ in water and to optimize the reaction kinetics. If properly catalyzed, the secondary 47 reaction pathway of the ORR, associated to the production of toxic hydrogen peroxide, 48 can be completely avoided. The best performing catalyst is platinum [13-17]. Pt is ap-49 plied at the surface of the cathode in such a way to ensure optimal contact with both the 50 electrode itself and the electrolyte. The resulting interface is the most critical one for fuel 51 cell technologies since it is associated to the triple-phase boundary, i.e. the zone where 52 protons, electrons and oxygen molecules must reach the catalyst sites to react [18-21]. In 53 this view the Gas Diffusion Layer (GDL) is a key component of fuel cells to manage dif-54 fusion of gaseous reactants, such as oxygen, to promote removal of excess water in prox-55 imity of the catalyst layer and, in MFCs, to minimize as much as possible the electrolyte 56 leakage [22]. The ideal GDLs must satisfy several properties, such as high gas diffusion 57 [23,24], good bending stiffness, continuous porosity, air permeability, water vapor diffu-58 sion, high surface area to volume ratio to ensure the water removal, good electrical and 59 electronic conductivity to ensure the proper electrons' transfer and suitable mechanical 60 stability [21]. For what concerns air-cathode single chamber microbial fuel cells (a-61 SCMFCs), commonly used GDLs are characterized by a backbone made of a carbon-62 based material acting as the electrode, which is then covered by the catalyst layer on one 63 side [25], and by a hydrophobic coating, typically based on polytetrafluoroethylene 64 (PTFE) on the side. PTFE is strongly hydrophobic and permeable to oxygen. These prop-65 erties can be very useful to design GDLs for MFCs since this polymer can act as a barrier 66 to avoid electrolyte leakage from the cell, while allowing oxygen diffusion, and contrib-67 uting to avoid excess of water, so preventing the cathode flooding [26-30]. Nevertheless, 68 the PTFE layer needs careful design in order to avoid any negative influence to the final 69 behavior of the cathode. Guerrini et al. [30] demonstrated that excess PTFE in GDLs for 70 open-air cathode MFCs, can make the electrode too hydrophobic preventing water from 71 reaching the catalytic sites, inhibiting the ORR reaction. Moreover, many works in the 72 literature, in the main fields of fuel cell technology, focused their attention on the GDLs' 73 structure, that could be a bottleneck for improving of functionality of this layer [18-30]. 74 Indeed, during last decades, nanostructured materials, gained increasing interest in the 75 design of GDLs to overcome the above-described limitations, ensuring optimized gas 76 diffusion, optimal water management and structural refinement [18, 31-32]. 77

The present work proposes the development of a novel nanostructured-gas-diffusion-78 layer (nano-GDL) to improve the overall behavior of a-SCMFCs with the aim to obtain 79 the best compromise among hydrophobicity and surface wettability properties of GDL. 80 To overcome all the limitations associated to the unprecise use of PTFE, which can in-81 duce an incomplete wetting of the cathode electrode, novel nano-GDLs were prepared 82 by the electrospinning process directly collecting on the same carbon-based electrode 83 two different nanofiber mats. The electrohydrodynamic process promotes optimal inter-84 action among the different layers, avoiding the need of a binder. The first layer (inner-85 layer) was made of cellulose nanofibers that play a crucial role to promote oxygen diffu-86 sion into SCMFC [29-30]. With the aim to improve the adhesion of this first nanostruc-87 tured layer to the carbon backbone, in the present work, we propose to create carbon-88 ized patterns into the cellulose nanofibers by direct laser writing. To this purpose, the 89 carbonized patterns were designed allowing the creation of graphene-like regions (i.e., 90 Laser Induced Graphene) combined with un-treated cellulose nanofibers which played a 91 key role ensuring the necessary hydrophilicity to improve water retention in proximity 92 of the active catalytic sites, thus avoiding any decrease of proton conductivity of the 93 electrolyte by dehydration [29-30]. The second layer (outward-layer) was based on poly-94 vinyl-fluoride (PVDF) nanofibers with the main purpose to prevent the electrolyte 95

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leakage, while allowing oxygen free to flow combined with a correct water removal 96 from cathode electrode. The design of new nano-GDL allowed exploiting all nanofibers 97 intrinsic properties, such as high surface ratio to volume, high continuous porosity, and 98 light weight, achieving thus a good oxygen diffusion in the proximity of the catalyst 99 layer, ensuring optimal surface wettability, and thus favoring the direct ORR while pre-100 venting the water flooding in correspondence of catalyst layer. We proposed the ideal 101 catalyst layer for ORR, based onto Platinum on carbon [35], directly deposited on the 102 inner side of carbon paper, on which both of two nanostructured layers were directly 103 collected. To investigate the good performances of SCMFCs, achieved when nano-GDLs 104 were employed, cathode electrodes with commercial gas diffusion layers, made of PTFE, 105 were used for comparison. We demonstrated the capability of a-SCMFCs with nano-106 GDLs to achieve a maximum current density equal to (132.2 ± 10.8) mA m⁻², an order of 107 magnitude higher than the one reached with commercial-PTFE, equal to (58.5 ± 2.4) mA 108 m⁻². To confirm the extremely/excellent performances, provided by nano-GDLs, we pro-109 pose an analysis of obtained results in terms of energy recovery, as already reported in 110 our previous work [36]. In line with the trend obtained by analyzing the current densi-111 ties, it is possible to state that nano-GDLs ensured the achievement of an energy recov-112 ery of 60.83 mJ m⁻³, one order of magnitude higher than the value obtained by commer-113 cial-PTFE (3.92 mJ m⁻³). All these latter results open the doors to the design of the whole 114 nanostructured cathode electrode in SCMFCs. To achieve this goals, nitrogen-doped car-115 bon nanofibers (N-CNFs) can be proposed as conductive carbon backbone, able to ex-116 ploit simultaneously good electrocatalytic properties for ORR, as deeply defined in our 117 previous work [11]. 118

2. Materials and Methods

2.1 Gas Diffusion Layer package and nanofibers synthesis

Nanostructured GDLs were obtained by deposition of nanofibers mats directly onto 121 carbon-based materials (Carbon Paper, purchased from Fuel Cell earth). To this purpose, 122 electrospinning process (NANON 01A electrospinning apparatus MECC, LTD) was in-123 volved to design nano-GDLs, guaranteeing the ability to connect two different nanofibers' 124 layers, without the use of a binder, suitable to connect all developed layer to the carbon 125 backbone. In this configuration, carbon paper pieces, cut in a square shape of (3x3) cm², 126 were used as counter electrodes during the electrospinning process, leading thus to obtain 127 cathode electrodes with the desirable geometric area for application in Microbial Fuel 128 Cells. Nano-GDLs were composed by two different layers. The first layer was based on 129 cellulose nanofibers, obtained by implementing an hydrolyzation process of cellulose ac-130 etate nanofibers [37-38]. Indeed, cellulose acetate nanofibers were immersed for 1h in an 131 ethanol-based solution containing 0.05M di NaOH. To guarantee a successful carboniza-132 tion process in ambient atmosphere, no subsequent washing is needed. In this way, it has 133 been possible to perform the laser writing step under ambient conditions, directly obtain-134 ing the LIG patterns from the cellulose nanofibers. This experimental approach improves 135 the adhesion of all nanostructured GDLs to the carbon backbone. CO₂ Laser Writing 136 (Pulsed CO₂ laser source, implementing by commercial Laser Scriber by Microla Optoe-137 lectronics S.r.l) was employed to occur the carbonization of cellulose nanofibers, as deeply 138 investigated in the literature [37-38]. In particular, the great advantage of CO2 laser writ-139 ing was identified by the capability to create carbonized patterns onto nanofibers mats, 140following different and desirable paths. We proposed the possibility to perform the LIG 141 step under ambient conditions, writing onto cellulose nanofibers carbonized patterns, 142 which led to improve the adhesion of all nanostructured GDLs to the carbon backbone. 143 The second layer was made of polyvinyl fluoride, PVDF-nanofibers, achieved by starting 144 a polymeric solution of 2g of PVDF (Mw=150 kDa, Sigma Aldrich) dissolved in a mixture 145 (1:1 v/v) of N-N Dimethylformamide (N-N DMF) and acetone. The deposition of PVDF 146 nanofibers is achieved to ensure the correct balance between hydrophilic properties and
 hydrophobic features, preventing possible leakage of electrolyte solution.
 For both nanofibers' mats, the electrospinning parameters were an applied voltage
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of 26 kV, a working distance of 15cm and a flow rate of 0.5 mL h-1.

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2.2 SCMFCs architecture and operation

The experiment was carried on using squared shape open-air cathode SCMFCs that we 154 discussed in previous articles [10-11]. A 3D printer (OBJET 30) was used to fabricate the 155 membrane-less cells, characterized by a single reaction chamber shared between anode 156 and cathode. The two electrodes were kept at a fixed distance thanks to an intermediate 157 septum, ensuring an inner volume of 12.5 mL. Both the electrodes have a squared shape, 158 with a geometric surface area close to 5.76 cm². They both were made of carbon paper 159 (CP, from Fuel Cell Earth, USA). To ensure maximum anodic stability, all the anodes of 160 the here proposed experiment have been obtained from a-SMFCs already running in our 161 Labs [36], characterized by anodic biofilms made of mixed consortia. For what concerns 162 the cathode electrodes, on the inner side of cathode electrode, standard platinum cata-163 lyst layer made of 0.5 mg cm⁻² of Pt/C (by Sigma Aldrich) and 5wt% of Nafion (Sigma 164 Aldrich) was applied [34]. On the outer side of cathode electrode, with the main purpose 165 to improve the triple phase boundary to ensure the direct ORR, and consequently in-166 creasing the overall devices' performance, three different GDLs were proposed and com-167 pared: i) the first one was made of a nanostructured GDL and was named nano-GDL: it 168 consisted into 2 layers of nanofiber mats, the first one is made of hydrolyzed acetate 169 nanofibers, on which a second layer of PVDF-nanofibers were deposited; ii) the second 170 one, defined as nano-LIG GDL, was based on two different layers of nanofibers: a layer 171 of cellulose nanofibers patterned by LIG and a PVDF-nanofibers layer; and iii) the third 172 material was composed by a Polytetrafluoroethylene (PTFE) layer, and it is referred to as 173 commercial-PTFE. A water-based solution containing 12 mM of sodium acetate was 174 used as the electrolyte, with sodium acetate serving as the carbon-energy source. Am-175 monium chloride (5.8 mM) and phosphate buffer saline solution (PBS) [10-12] were 176 added to the promote the metabolic activity of microorganisms. Titanium wires were 177 employed for electrical contact and a multichannel data acquisition unit (Agilent 34972 178 A) was used to monitor the output voltage from the cells. Titanium wires were threaded 179 through the polymeric frame, so that once the frame is correctly positioned inside the 180 cathode compartment and exploiting the mechanical pressure obtained when closing the 181 cell, an optimum electrical contact is ensured. An external load of $1k\Omega$ was applied to 182 each cell. Indirectly, through the first Ohmic Law, current values were defined. Moreo-183 ver, a current density trend was obtained by dividing each current value for the geomet-184 ric area of the electrode, equal to 5.76 cm². All the devices were operated in fed-batch 185 mode, thus ensuring the electrolyte replacement when the output voltage dropped to 186 0V. All the experiments were conducted in duplicate. 187

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). Through the analysis of FESEM images allowed defining the preservation of nanostructures also after the LIG process, implementing to improve the adhesion of both nanofibers' layers, components of the new gas diffusion layer GDL. Moreover, to confirm the effective role of high continuous porosity onto diffusion of oxygen species inside the devices and onto the balance between water retaining and removing, FESEM images were analyzed with an imaging software (ImageJ).

Final porosity of both samples, nano-LIG 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}).

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

Furthermore, to confirm the effectivennes of imageJ analysis performed on FESEM images, Brunauer–Emmett–Teller (BET, Micrometrics, ASAP 2020 Plus) measurements were implemented to define the specific surface area of nano-LIG GDLs, leading thus to evaluate the porosity distribution of the nanostructured layers.

To evaluate how nano-LIG GDL can affect SCMFCs performance, improving it with respect to the performance achieved with nano-GLD and commercial PTFE, Linear Sweep Voltammetry (LSV) characterizations were defined by using Palmsens potentiostat (Palmsens4, Netherlands)). LSV characterizations were performed at the end of experimental study, ranging the voltage from open circuit to a short circuit at a rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS), using a Palmsens potentiostat, were provided to define electrocatalytic features of cathodes. EIS analysis was performed applying an external fixed resistor of 100Ω [12], using a sinusoidal signal with an amplitude of 25 mV and frequency spanning between 150 kHz and 200 mHz.

The equivalent circuit of Scheme 1 was used to fit the experimental data from EIS, in 213 such a way to quantitatively evaluate the following electrical parameters: i) R1, i.e. the 214 series resistance, accounts for electrolyte and wiring resistances; ii) R2 and R3 are associ-215 ated to the resistances to charge transport inside the electrode and to the charge transfer 216 at the electrode/electrolyte interface, respectively. Due to porous nature of cathode elec-217 trodes, constant phase elements, Q1 and Q2 are used to model the corresponding double 218 layer capacitances [12].; and finally, iii) Warburg element was included to model low 219 frequency feature, commonly corresponding to the species diffusion. 220



Scheme 1. Equivalent circuit used to fit the impedance spectra

3. Results and Discussion

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

Aiming to perform the LIG step in ambient conditions, to facilitate the fabrication pro-225 cess to scale it up, the main results was achieving by the definition of proper conditions 226 for a graphitization avoiding the burning the material. Indeed, to ensure the carboniza-227 tion of cellulose nanofibers, high temperatures must be reached, at which basically these 228 synthetic polymers burned in the presence of oxygen. All these limitations demand the 229 development of a polymeric nanofibers treatment capable of allowing and guaranteeing 230 the carbonization of the nanofibers themselves under ambient conditions, without the 231 implementation of technical gases, such as argon or nitrogen, typically employed during 232 the standard carbonization process [36]. The obtained results highlighted how the 233 deacetylation step, usually involved to transform the cellulose acetate nanofibers into 234 cellulose nanofibers, if not followed by subsequent washing in deionized water, resulted 235 to be pivotal to ensure the carbonization of nanofibers under ambient conditions. It was 236

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possible to demonstrate that the presence of NaOH salts onto cellulose nanofibers re-237 sulted to have a key role to promote carbonization of cellulose nanofibers. As shown in 238 Figure 1a, the presence of NaOH salt, decorating cellulose nanofibers mats, was con-239 firmed by FESEM images, whereas on the contrary, NaOH was completely disappeared 240 after the implementation of LIG process conducted in ambient condition, as represented 241 in Figure 1b). Moreover, Figure 1b) allowed demonstrating the preservation of 242 nanostructures also after the LIG process applied to create carbonized patterns onto nan-243 ofiber mats. 244



Figure 1. a) Morphological properties of cellulose nanofibers after deacetylation process, confirming the presence of NaOH salts onto nanofibers mats; b) morphological properties of carbonized cellulose nanofibers, guaranteeing the preservation of nanostructures also after the LIG process involved to create carbonized patterns onto nanofiber mats

This result can be explained by considering the hypothesis that the NaOH salts were able 250to sublime during the CO₂ laser writing process, ensuring the formation of an oxygen-free 251 atmosphere during the process itself, leading thus the complete transformation of cellulose nanofibers into carbon-based nanofibers. With the main purpose to confirm the capability of CO2 laser writing to transform into laser-induced Graphene (LIG)- nanofibers the initial cellulose nanofibers, Raman characterization was employed. As reported in Figure 2, it is possible to detect an achieved graphitization of material as evidenced by the presence of the G peak at about 1580 cm⁻¹. The graphitization is certainly partial, and the pres-257 ence of a pronounced 'neck' between the G peak and the D peak (at about 1350 cm⁻¹) indi-258 cates the presence of groups of various kinds bound to the graphitic lattice. These groups can be defined as oxygen-containing functional groups due to the partial graphitization of the starting cellulose nanofibers [37]. For what concerned the 2D band peak, this peak 261 is not detectable due to the low degree of graphitization, leading thus to exclude this part 262 of spectrum, because it does not provide any further information. 263

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Figure 2. Raman spectrum of carbonized patterns created onto cellulose nanofibers thanks to the implementation of CO₂ laser writing. The presence of G-band at 1580 cm⁻¹ confirmed the achieved graphitization of nanofibers, that remain partial, highlighting the presence of oxygen-containing functional groups as confirmed by the 'neck' between the G peak and the D peak (at about 1350 cm-1)

Moreover, the morphological properties of the whole nano-LIG GDLs, obtained after the 270 deposition of PVDF-nanofiber layers on the cellulose nanofibers, previously carbonized 271 through CO₂ laser writing process, were investigated and reported in Figure 3a), high-272 lighting thus the pore distribution in these samples. Indeed Nano-LIG GDL are character-273 ized by pores with dimensions in the range of few micrometers, leading thus to exhibit a 274 higher surface area to volume ratio than the one obtained with commercial gas diffusion 275 layers, commercial-PTFE (see Figure 3b). The ImageJ software allowed indirectly evalu-276 ating the porosity distribution into Nano-LIG GDL, comparing it with the one achieved 277 with commercial-PTFE. To this purpose, the porosity distribution of all samples was de-278 termined by applying Equation 1. Figure 3c) allowed confirming that the porosity distri-279 bution of Nano-LIG GDL, close to 77%, results to be higher than the one when commer-280 cial-PTFE was applied (equal to 25%). High porosity distribution values are in line with 281 the results achieved by determining specific surface area of whole nano-LIG GDLs by im-282 plementing Brunauer-Emmett-Teller (BET) measurements. Nano-LIG GDLs showed a 283 specific surface area of 18.94 ± 0.05 m²/g. Moreover, from BET measurements, it is possible 284 to define the pores distribution inside the whole nanostructured layers. Nano-LIG GDLs 285 showed pores dimension in the range from 2nm to 10 nm, leading thus to define that 286 Nano-LIG GDLs is a micro and mesoporous material. High continuous porosity showed 287 in Figure 3c), greater than the one achieved by commercial-PTFE, can positively affect the 288 diffusion of oxygen from outside towards the catalytic active sites, leading thus to im-289 prove the triple phase boundary. These intrinsic properties of nanofibers with particular 290 attention on their high continuous porosity can play a pivotal role into the enhancement 291 of oxygen diffusion in proximity of triple contact zone, ensuring thus a better oxygen 292 transport in proximity of catalytic active sites. 293

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Figure 3. a) Morphological properties of nanostructured-LIG GDLs, confirming high porosity of
samples, as highlighted from higher magnification, underlined by red box; b) Morphological prop-
erties of commercial-PTFE; c) Evaluation of porosity distribution of nanostructured-LIG GDLs com-
pared with the one reached with commercial-PTFE.295
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3.2 SCMFCs performance

As previously described, anodes electrodes, on which a microorganisms proliferation 300 occurred were obtained by preceding experiments [36]. For all cathode electrodes plati-301 num is involved as catalyst, while nano-LIG GDL, nano-GDL and commercial-PTFE 302 were compared, to evaluate how all the properties of both nano-GDLs can affect the 303 overall performance of SCMFCs. Figure 4 represents the current density trends over 304 time. Nano-LIG GDL reached a maximum current density equal to (151.2 ± 15.5) mA m-305 2, which is double of the one reached with Nano-GDL, confirming how the presence of 306 conductive patterns played a pivotal role to ensure the design of a better performing Gas 307 Diffusion Layer. Moreover, Figure 4 also highlighted that nanostructured arrangement 308 of Gas diffusion Layers allowed achieving improved overall SCMFCs performance, if 309 compared with commercial-PTFE (maximum current density close to (58.5±2.4) mA m 310 2), used as reference material. Since the anodes electrodes resulted to be formally identi-311 cal for all devices, it is possible to attribute the different power production of SCMFCs 312 directly to the development of diverse nano-GDLs onto cathode electrodes. 313

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Figure 4. Comparison of average current density trend of SCMFCs with nano-GDL and nano-LIG GDL compared with the one achieved by SCMFCs made of commercial-PTFE

This latter result allowed confirming the key role of nano-LIG GDL with a great interest 318 onto the presence of conductive patterns, creating through the CO2 laser writing, able to 319 further improve overall SCMFCs' performance. Indeed, the presence of conductive pat-320 terns could improve the contact between the whole nanostructured GDL and the carbon 321 backbone, allowing the enhancement of the triple contact zone, oxygen diffusion in proximity of catalytic active sites and, at the same time, thanks to the presence of hydrophilic cellulose-NFs layers, 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. In line with the 326 obtained results, we performed LSV and electrochemical characterizations onto SCMFCs that showed nano-GDL, nano-LIG GDL and commercial-PTFE. 328 Both of SCMFCs devices reach a similar open circuit voltage (OCV) close to 0.4V, while SCMFCs with nano-LIG 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 nano-LIG 331 GDL can affect and favor the direct ORR, ensuring the best oxygen diffusion into 332 SCMFCs, the variation of total cathodic resistance over time was investigated through 333 EIS. Typical Nyquist plots are represented in Figure 5b), comparing nano-LIG GDL and 334

commercial one. The curves obtained by fitting procedure are overlaid on the experi-

mental data (see Figure5b). Table 1, on the contrary, summarized all resistance values.

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Figure 5. a) Polarization curves obtained by LSV characterization. Potential vs. current density338curves (left axis, straight lines) and power density vs. current density (right axis, dash lines) curves339of all SCMFCs. b) Typical impedance spectra of nano-LIG GDL (red dot and line), nano-LIG (blue340dot and line) and commercial-PTFE (black dot and line).341

As highlighted in Figure 5b), all SCMFCs show a similar value of series resistance R1, 343 independently of cathode electrodes. This is to be expected, since electrolyte, wires and 344 electrical connection are identical for all SCMFCs. Moreover, the lower is the charge 345 transfer at the electrode/electrolyte interface R₃, higher is the capacity of cathode elec-346 trode to ensure a faster electrons flow. This result demonstrates the effectiveness of 347 nano-LIG GDL to ensure an enhancement of oxygen diffusion, improving consequently 348 the occurring of direct-ORR and the overall SCMFCs performance. A similar trend is 349 observed for the transport resistance R₂, which is visible in the high-frequency smaller 350 arc sketched in Figure 5b). 351

A lower R2 defines an increasing of electrode transport properties and since all other352aspects of cathode electrodes are the same, it is possible to confirm how nano-GDL re-353sults to be more efficient in carrying out ORR.354

Table 1. Typical resistance values (R1, R2 and R3) calculated from the fitting procedure on Electro-
chemical Impedance Spectroscopy (EIS) data. For each parameter, the maximum variation observed
between three nominally identical Microbial Fuel Cells (MFCs) was 10%.355357

Cathode electrodes	R1 [Ω]	R2 [Ω]	R3 [Ω
Nano-LIG GDL	44.3	12.04	38.4
Nano-GDL	54.17	24.69	128.8
Commercial-PTFE	36.9	25.7	50.5

Moreover, in line with all obtained results, the analysis performed in terms of energy 359 recovery parameter, defined as ratio of generated power integral and the internal volume 360 of devices, allow evaluating the overall SCMFC performance. SCMFCs with a nano-LIG 361

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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-3 363

4. Conclusion

In the present work, nano-LIG 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, nanofiber mats were directly collected on carbonbased materials, used as cathode electrodes, without the necessity of binder to bond GDL with the carbon backbone. Morphological analysis gave evidence of a higher porosity obtained with nano-GDL, than that reached using commercial-PTFE.

All obtained results demonstrate that nano-LIG GDLs are effective in improving a-372 SCMFCs performance, showing a maximum current density value that doubles the one 373 obtained using standard PTFE. Since the changes introduced among the cathodes used in 374 this work are referred to the new nano-LIG GDLs, it is possible to confirm that the ob-375 served improvement is related to use of nanostructured materials for GDL. All the ob-376 tained results demonstrate the effectiveness of nano-LIG GDL to ensure an enhancement 377 of oxygen diffusion, consequently enhancing the direct-ORR and thus the final perfor-378 mance a-SCMFCs. 379

Author Contributions: Conceptualization, G.M and M.Q.; methodology, G.M. and M.Q.; validation,381formal analysis and investigation, G.M.; resources, M.Q and C.F.P.; data curation, G.M.; writing382original draft preparation, G.M.; writingreview and editing, T.S., M.Q and C.F.P.; visualization,383G.M and M.Q; supervision, project administration and funding acquisition, M.Q and C.F.P. All authors have read and agreed to the published version of the manuscript.385

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