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Increasing bioelectricity generation in microbial fuel cells by a high-performance cellulose-based membrane electrode assembly

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6 **Increasing Bioelectricity Generation In A Single Chamber**  
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10 **Microbial Fuel Cell By A Novel Monolithic Structure**  
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13 **Membrane Electrode Assembly Based on Low Cost**  
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17 **Bacterial Cellulose and Cheap Nano-Zycol**  
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## Abstract

Herein, a novel monolithic membrane electrode assembly (MEA) air-cathode based on bacterial cellulose (BC), conductive multi-walled carbon nanotubes (CNT) and hydrophobic nano zycosil (NZ) was fabricated for Microbial fuel cell (MFC). BC as a nano-celluloses with oxygen barrier property can prepare anaerobic condition in the sludge. Binder-less coating of CNT on BC avoids expensive binders like poly-tetra fluoro ethylene (PTFE) and Nafion. Also, NZ is here proposed as a very cheap organosilane to make BC's surface hydrophobic and prevents anolyte leakage. It was coated on BC by an easy, fast and direct approach without post treatment. Diluted NZ increased the water contact angle (WCA) from 49° (BC) to 85° (BC-NZ) and balanced hydrophobicity and humidity of BC. Electrochemical performance of the BC-CNT-NZ was compared to PTFE- carbon cloth gas diffusion electrode (GDE) in a single chamber MFC (SCMFC). BC-CNT-NZ produced maximum pulse power density of 1790 mW/m<sup>2</sup> that was approximately two times higher than that obtained by GDE (920 mW/m<sup>2</sup>). Also, the capacitance of the MEA was 65 mF and much higher than the value for GDE (0.73 mF). Thus, BC-CNT-NZ is suggested as a high performance and cheap substitute for typical hydrophobic PTFE based GDEs in SCMFC.

**Keywords:** Bacterial cellulose; Nano zycosil; Carbon nanotubes; Monolithic; Membrane electrode assembly; Microbial fuel cell

## 1. Introduction

Microbial Fuel Cell (MFC) is an emerging technology in the field of sustainable bioelectricity, wastewater treatment and bioelectronics [1, 2]. In MFCs, bacteria as biocatalysts decompose and consume a wide range of organic molecules, simple or complex, present in waste water, while releasing electrons through an external loading, towards the cathode[3, 4]. At the cathode side, electrons are involved in the oxygen reduction reaction (ORR)[5, 6]. In single chamber MFCs (SCMFCs), the air-breathing cathode prevents

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4 anolyte leakage, and also provides ORR sites [7]. Therefore air-cathode plays a vital role in MFC's  
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6 operation. A large variety of materials and structures have been employed in air-cathode fabrication process  
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8 [8, 9]. Typical air-breathing cathodes feature a membrane electrode assembly (MEA) design. MEA key  
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10 components are: i) the conductive substrate where the electrocatalytic reduction of O<sub>2</sub> takes place, and ii)  
11  
12 the hydrophobic layer. Carbon paper and carbon cloth are introduced as commercial conductive substrates  
13  
14 coated by a mixture of carbon and poly-tetra fluoro ethylene (PTFE) to build gas diffusion electrode (GDE)  
15  
16 air-cathodes [10]. High cost PTFE is used to bind the carbon mixture to the substrate. Furthermore, it makes  
17  
18 the GDE surface hydrophobic, and hence, prevents leakage [11]. In addition to conductive substrates, non-  
19  
20 electrical conductive ones are also used to fabricate MEA air cathodes. A variety of ultrafiltration  
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22 membranes, proton, cation and anion exchange membranes can be used as MEA substrates. MEA's  
23  
24 substrate plays a vital role as a barrier to anolyte leakage and oxygen cross-over and affects proton or cation  
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26 exchange for MFC operation[12]. Scientists are making effort to find low-cost air cathodes based on cheap  
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28 materials and obtained by environmentally friendly processes to make MFC technology more practical.  
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34 Cellulose has caught the eye of scientists because it is the most widely available biopolymer in the world  
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36 [13, 14]. Permeability of oxygen through pure nano cellulose materials is very low [15] and it is necessary  
37  
38 to mitigate oxygen crossover by air cathode in MFC [16]. Among nano cellulose materials, bacterial  
39  
40 cellulose (BC) has received extensive attention due to its three-dimensional porous nano-structural network,  
41  
42 high purity, flexibility, high mechanical strength, and excellent tear resistance in aquatic environments[17,  
43  
44 18]. These novel features make BC an excellent green substrate for electrode fabrication in MFC.  
45  
46 Conductive polymers coated BC were exploited as cheap bio-anodes in a double chamber MFC (DCMFC),  
47  
48 which gave much higher power density response rather than graphite [19, 20]. In other work, flexible  
49  
50 conductive BCs were coated with CNT and Gum Arabic binder by drop casting method and low sheet  
51  
52 resistance of 1 Ω.cm was reported [21]. CNT has been investigated as an effective nano carbon in MFCs  
53  
54 [22, 23]. In recent years, a great interest has being seen in exploiting BC in biofuel cells (BFCs). BC-CNT  
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56 composites were prepared by vacuum filter method and were utilized as anode and cathode in two chamber  
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4 enzymatic fuel cells [24]. Moreover, a BC based proton exchange membrane (PEM) was fabricated by  
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6 Vilela et al. with poly sulfonic acid treatment and used it in a SCMFC with a hydrophobic micro porous  
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8 layer (MPL)-carbon cloth air-cathode [25]. The internal resistance of the MFC was high and the open circuit  
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10 voltage (OCV) of the cell was low. The reason may be the lack of proper BC's connection to the carbon  
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12 cloth in that work.  
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16 Besides abovementioned properties of BC like oxygen cross-over barrier and proton conductivity, a  
17  
18 hydrophobic surface of BC is vital for eliminating water leakage to reach an excellent MEA-air cathode  
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20 based on BC-CNT as a cheap alternative to high cost carbon cloth and PTFE. Several methods were applied  
21  
22 to make cellulose hydrophobic such as: acetylation [26] and silanization of cellulose with organosilane  
23  
24 groups by complex methods [27-29]. Apart from the materials, nano-zycosil (NZ), a diluted solution of  
25  
26 hydroxyalkyl-alkoxy-alkylsilyl, has been introduced as a cheap and commercially accessible organo-silane.  
27  
28 Because of its low cost, NZ is suitable for industrial applications [30, 31]. In this study, for the first time  
29  
30 BC-CNT-NZ is fabricated as a monolithic MEA in SCMFC. In all previous studies by the scientists, BC  
31  
32 was used only as the membrane in presence of PTFE based-GDEs. Here, one side of BC was coated with  
33  
34 CNT by using vacuum filter method with no binder. Consequently, only one side of BC's surface became  
35  
36 conductive. The conductive surface was in front of the air. The other side of BC was coated with NZ to  
37  
38 make a hydrophobic surface and prevent leakage of the sludge in SCMFC. Various characterization  
39  
40 methods were applied to investigate the properties of BC-NZ surface as a novel hydrophobic BC membrane.  
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42 To the best of our knowledge, it is the first time that BC and NZ are used for the fabrication of MFC air  
43  
44 cathode. The monolithic structural MEA was expected to show excellent performance in MFC. Resistance,  
45  
46 capacitance, catalytic activity and generated power density of the MEA were studied by several  
47  
48 electrochemical experiments.  
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## 53 54 55 **2. Materials and methods**

### 56 57 58 **2.1. Fabrication of BC-CNT-NZ MEA**

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4 As can be seen in Fig.1 A, a solution containing 10 mg of CNT (Neutrino Noavarane Nano, Iran) and 25  
5 mg of SDS surfactant in 25 mL of Milli-Q water was mixed under 15 min ultrasonic to reach a homogeneous  
6 solution of CNT. Thereafter, the solution was poured on BC membrane (Nano-Novin Polymer, Iran) to  
7 cover BC by vacuum force of Buchner [32]. Then, the CNT coated BC was placed in ambient temperature  
8 for complete drying. Uncoated surface of BC-CNT was covered by NZ-water solution (1:5, v/v) (Zydex  
9 Industries, India) with a painting brush and left to dry overnight to yield the hydrophobic BC-CNT-NZ.  
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## 18 **2.2. Characterization of BC-CNT-NZ**

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21 NZ coating on BC was evaluated by Attenuated Total Reflectance Fourier Transform Infrared spectroscopy  
22 (ATR-FTIR) device (Brucker, Germany). Crystallinity was investigated by x-ray diffraction (XRD)  
23 (Philips, Germany) and quantified by the Segal equation [33]. Field Emission Scanning Electron  
24 Microscopy (FESEM) (TESCAN, Czech Republic) was utilized to investigate the surface morphology.  
25 Energy-dispersive x-ray (EDX) (TESCAN, Czech Republic) spectroscopy measurements provided the  
26 atomic percentage of the elements. Atomic force microscopy (AFM) (Philips, Germany) was used to  
27 calculate the average roughness of the surface (by Nanosurf Easyscan software) [34], Thermo-gravimetric  
28 analysis (TGA) (TA Instruments, USA) was carried out to evaluate thermal stability of materials . Contact  
29 angle (Sharif Solar, Iran) measurements were performed to investigate the effect of NZ coating on  
30 hydrophobicity.  
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## 44 **2.3. SCMFC and incubation**

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47 A cubic single-chamber MFC (SCMFC) with four windows for different air-cathodes and 250 ml working  
48 volume was used in this research (Fig.1 B). Carbon brush (wrapped around two titanium wires with  
49 diameter of 2 cm and height of 4 cm) was embedded in the centre of the chamber as anode electrode. BC-  
50 CNT-NZ and commercially GDE were used as air-cathodes. The distance of anode from both GDE and  
51 new MEA was the same. The system was incubated by anaerobic sludge from hydrolysis stage at biogas  
52 plant (Biotech. Sys. Srl, Bologna, Italy). The sludge was diluted 50:50 V/V by phosphate buffer solution  
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4 (0.1 M PBS). The surface of each cathode was 2.5 cm in 2.5 cm. A 1 kΩ external resistance was connected  
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6 to MFC for a week for biofilm formation. Cathode current collector was from stain-less steel mesh. To seal  
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8 the air-cathode windows of the chamber, the electrode and current collector were sandwiched between two  
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10 frames of silicon gaskets. The anode inlet was closed by a silicon cap.  
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#### 14 **2.4. Electrochemical tests**

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17 For all the electrochemical tests, a potentiostat/galvanostat (Biologic Science Instruments, France) at LEME  
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19 was utilized.  
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22 The catalytic activity of BC-CNT-NZ and commercial GDE was evaluated in SCMFC in three-electrode  
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24 mode, i.e. using the cathodes as working electrode, the anode as counter, and inserting an Ag/AgCl  
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26 reference electrode in the SCMFC chamber.  
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30 Linear sweep voltammetries (LSV) were carried out by rotating disk electrode (RDE) at different rpm to  
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32 investigate the ORR catalytic activity of CNT in circum-neutral electrolyte. In RDE test, the working  
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34 electrode was a glassy carbon (GC) RDE coated with CNT following the procedure described in ref. [35].  
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37 The experiment was done in a standard-three electrode cell filled by 50 ml PBS (0.1 M, pH=7.6) saturated  
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39 with oxygen before measurements. A Pt counter electrode and an Ag/AgCl reference electrode were used.  
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42 The LSV curves were analysed to give the Koutecky-Levich (K-L) and Tafel plots (Eq1 and Eq2):  
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$$45 \frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \beta \omega^{\frac{-1}{2}} + \frac{1}{j_K} \quad (1)$$

$$48 \log j_K = \gamma \eta + \log j_{K_0} \quad (2)$$

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53 Where  $j_L$ ,  $j_K$  and  $j$  are limiting, kinetic and measured currents densities respectively.  $\beta$  is the slope of K-L  
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55 plot and  $\omega$  represents the angular velocity of electrode. Also,  $\gamma$  is the slope of Tafel plot and  $\eta$  is measured  
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57 over-potential[36].  
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7 Additionally, LSVs were run in two-electrode mode. In this case, the working electrodes the BC-CNT-NZ  
8 and GDE cathodes. The anode brush was used as counter and reference electrode.  
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12 The polarization curve of the cell ( $V_{\text{cathode}}-V_{\text{anode}}$  vs. current density plot) were analyzed to calculate the  
13 output power density (P) by Eq.3:  
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$$15 \quad P = \frac{(V_C - V_A) \times I}{A_c} \quad (3)$$

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22 Where  $V_C$ ,  $V_A$ ,  $I$  and  $A_c$  represent cathode (V) and anode (V) potentials, cell's current (mA) and cathode  
23 surface area (m<sup>2</sup>).  
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27 During the cell LSV, to evaluate the single electrode polarization behavior, the electrode potential was  
28 simultaneously monitored vs Ag/AgCl in parallel. LSV scan rate was 0.2 mV.s<sup>-1</sup>.  
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33 Cyclic voltammetry was performed to evaluate the capacitive behavior of the cathodes. Scan rate was 10  
34 mV s<sup>-1</sup> and the potential window was -0.3V to 0.3V vs Ag/AgCl. Capacitance was calculated by the slope  
35 of the plot of the current integrated over time vs. electrode potential. EIS of cathodes was performed in the  
36 frequency range 100 KHz to 20 mHz at OCV. Both CV and EIS were carried out by a three electrode-setup  
37 in SCMFC filled with the sludge.  
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42 For Galvanostatic (GLV) test, different pulse current ( $I_{\text{pulse}}$ ) were imposed to discharge MFC in various  
43 pulse times ( $t_{\text{pulse}}$ ): 0.1s, 0.5s, 1s and 2s. After each discharge, the SCMFC was left to rest in OCV until a  
44 stable voltage was reached. In this method, cell voltage, anode and cathode potentials were recorded versus  
45 reference electrode (Ag/AgCl) and plotted vs. time. The pulse power ( $P_{\text{pulse}}$ ) was calculated by the cell GLV  
46 discharge according to Eq.4 [37-39]:  
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$$50 \quad P_{\text{pulse}} = (I_{\text{pulse}} * \int_0^t V dt) / t_{\text{pulse}} \quad (4)$$

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### 3. Results and discussion

#### 3.1. Surface Chemistry of BC-NZ

ATR-FTIR spectra of BC and BC-NZ films are reported in Fig.2 A. To reach a complete and qualitative comparison by FTIR spectra, the absorbance range was splitted to 4000-2500  $\text{cm}^{-1}$  and 1500-500  $\text{cm}^{-1}$ . A successful treatment of BC by NZ was found by the bands that can be detected at 775  $\text{cm}^{-1}$  and 1270  $\text{cm}^{-1}$  which can be attributed to bending vibrations of Si-CH<sub>3</sub> [28]. Additionally, stretching vibration of Si-CH<sub>3</sub> was visible by a small peak at 2966  $\text{cm}^{-1}$  [27, 40]. The latest peak located near 3000  $\text{cm}^{-1}$  provided evidence of the hydrophobic feature of BC. Also, the sharp signal between 1025  $\text{cm}^{-1}$  and 1035  $\text{cm}^{-1}$  can be attributed to Si-O bond [41]. In this region, it can be observed even a signal related to C-O deformation of cellulose (overlapping with Si-O of alkoxy group). Therefore, the normalized intensity of the peak at 898  $\text{cm}^{-1}$  for both BC and BC-NZ was compared and resulted 1.26 and 1.42 for BC and BC-NZ, respectively. As a consequence, increased intensity of the peak for BC-NZ was related to Si-O bond.

The fingerprint region between 1500-700  $\text{cm}^{-1}$  is of great importance in identifying structural changes of BC. Crystalline structure of BC was surveyed by two main indexes: total crystalline index (TCI) and lateral order index (LOI) [42, 43]. TCI and LOI were calculated by the ratio of  $A_{1372}/A_{2920}$  and  $A_{1430}/A_{898}$  respectively for both BC and BC-NZ. Bands at 1430  $\text{cm}^{-1}$  and 898  $\text{cm}^{-1}$  are representatives for crystalline and amorphous structure of BC[44]. Decrease in both LOI and TCI (Table 1) showed that a slight reaction between BC and nano zycosil has degraded a little the ordered structure of BC and its crystallites. Additionally, hydrogen bond index (HBI) which is defined as  $A_{3340}/A_{1330}$  was evaluated for both samples and then no noticeable change in HBI was observed (Table 1). Hence, the change in -OH group of BC was not significant. This behavior was mentioned earlier by Zanini et al. and Sai et al. for silanized cellulose [27, 45].

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4 Besides ATR-FTIR spectra, EDX analysis (Fig.2 B) was also performed to study atomic distribution on the  
5 surface of BC-NZ. The results showed 2.43% of surface atoms were Si. Additionally, by EDX mapping, it  
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7 was found that a homogenous coating of Si atoms occurred on BC's nano fibers. As it was mentioned, the  
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9 main reason of NZ coating was making a hydrophobic surface of BC.  
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### 14 **3.2. Crystallinity and thermal stability of BC-NZ**

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17 BC crystallinity was proven by the presence of the diffraction peaks at  $2\theta$  22.8°, 17.8° and 15° corresponding  
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19 to the planes 200, 110 and 110 (Fig.2 C) respectively [19, 20]. To investigate the effect of NZ on BC  
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21 nanofibers, the crystallinity of both pure and treated BC was calculated by Segal equation. Crystallinity of  
22  
23 92% and 87% for BC and BC-NZ indicates a negligible effect of silane groups on BC crystal structure. This  
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25 result confirmed the small decrease in TCI and LOI detected by ATR-FTIR spectra and commented in the  
26  
27 previous section. Accordingly, both FTIR and XRD analyses verified each other.  
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32 TGA and its differentiation (DTG) curves of BC and BC-NZ are displayed in Fig.2 D. Below 100°C, the  
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34 TGA curves exhibited a weight loss associated with the evaporation of sample's moisture (3.5%). The main  
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36 BC' degradation took place at the range of 320 to 340°C. DTG curves showed that after treatment by NZ,  
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38 the maximum rate of BC's decomposition occurred at higher temperature (it shifted from 321°C for BC to  
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40 338°C for BC-NZ). Furthermore, the rate was smaller in the case of BC-NZ. Hence, thermal analysis  
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42 suggests that silane groups of NZ improved the thermal stability of BC's nano fibers. This result is in  
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44 agreement with previous BC silanization [27].  
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### 48 **3.3. Surface morphology, hydrophobicity, roughness and barrier properties of BC-NZ**

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51 FE-SEM images of BC before and after modification are visible in Fig.3. By comparing Fig.3 (A and B)  
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53 corresponding to bare BC and BC-NZ, it is obvious that BC' surface was covered considerably by NZ and  
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55 also the pores between fibres became smaller. Therefore, the morphology change shown in FESEM  
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57 suggests that treatment with NZ should improve the barrier property of BC. WCA as a criteria for  
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59 hydrophobicity was measured. An appreciable change was seen between WCA of bare (49°) and NZ treated  
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4 BC (85°) (insets of Fig.3 (A and B)). Higher WCA resulted in higher hydrophobicity and also improved  
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6 water leakage barrier of BC-NZ membrane. It is noticeable that 98% w/w of bare BC in wet state is formed  
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8 from water. Hence, BC without surface treatment has considerable leakage followed by its high affinity to  
9  
10 water and cannot be applied as a separator or membrane in air-cathode fabrication. FE-SEM images and  
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12 WCA confirmed successful surface treatment of BC by NZ. Additionally, AFM images (Fig. 3 (C and D))  
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14 showed that surface roughness was decreased from 45.66 nm for BC to 32.51 nm for BC-NZ. Also, the  
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16 values of valley depth and peak height showed decrease after treatment of BC with NZ. It means that BC's  
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18 pores with micron scale have become filled with NZ[46, 47]. It was also clear in FESEM images. Hence,  
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20 all AFM, FESEM and WCA results implied on hydrophobic features of treated BC.  
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25 It is necessary to know BC's desired hydrophobization degree for MEA. A balanced WCA presents better  
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27 performance. This theory was brought up previously for GDL of air-cathode by Ci et al [11]. To the best of  
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29 our knowledge, here it is the first time that the theory is considered for MEAs. As can be seen in Fig.4 A,  
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31 ORR needs sufficient protons, electrons and oxygen. For introduced BC-CNT-NZ, protons cross BC-NZ  
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33 to meet electrons and oxygen at the interface of BC and CNT. High WCA (130°) decreases total protons  
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35 reaching the BC-CNT interface and therefore makes a limiting factor to ORR. On the other hands, low  
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37 WCA (49°) results in leakage and therefore lower concentration of oxygen in ORR sites (because of lower  
38  
39 soluble oxygen in water phase rather than air). Thus, a balanced WCA (85°) not only provides sufficiently  
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41 proton transfer in reaction sites by BC but also prevents leakage by NZ coating. Furthermore, performance  
42  
43 of BC-NZ as a barrier to air oxygen penetration was evaluated by measuring dissolved oxygen (DO) (by  
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45 DELTA OHM, Italy) versus time and was compared with the measured amount of PTFE based GDE and  
46  
47 Mylar (as control) (Fig. 4 B). The experiment was carried out in three similar cells with BC-NZ, PTFE and  
48  
49 Mylar respectively, all filled by PBS (initially purged with nitrogen for 30 minutes to remove DO). After 9  
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51 h, the cell with BC-NZ showed a plateau in low DO while the GDE showed a growing trend. Hence,  
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53 excellent anaerobic condition was provided by new MEA. Indeed, NZ provided both hydrophobicity and  
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55 great barrier property against oxygen diffusion. It is a positive point for use of NZ rather than PTFE. The  
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4 other parameter in SCMFC is anolyte evaporation rate from air-cathode surface. For this purpose, the three  
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6 cells were weighted in a period of 90 h to find weight-loss associated with evaporation of PBS (Fig. 4 C).  
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8 The behavior of both BC-NZ and PTFE based GDE was almost same. A little higher rate of BC-NZ may  
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10 be explained by the mentioned balance between hydrophobicity and humidity in BC-NZ.  
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### 14 **3.4. Electrochemical properties of BC-CNT-NZ compared to commercial GDE**

#### 15 16 17 **3.4.1. Impedance spectroscopy study**

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20 EIS spectra of BC-CNT-NZ and commercial GDE are demonstrated in Fig.5. The Nyquist diagram of BC-  
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22 CNT-NZ span in an impedance range that is much smaller than that of the GDE and is not visible without  
23  
24 magnification. At 20 mHz, real and imaginary parts of impedance were 114.283  $\Omega$  and 122.28  $\Omega$   
25  
26 respectively for BC-CNT-NZ while GDE showed much higher resistances, 2.8 k $\Omega$  and 10.8 k $\Omega$   
27  
28 respectively. At the high frequency range, BC-CNT-NZ Nyquist plot features a semicircle that can be  
29  
30 related to the electronic connection between the CNT and the stainless steel current collector. In the middle  
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32 frequency range, a line with a slope approaching 45° is representative of ion diffusion in to the BC-CNT-  
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34 NZ porous architecture, and can be modelled with a Warburg element. Additionally, in low frequency  
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36 region, BC-CNT-NZ's capacitive behavior appears much more prominent rather than its Warburg part. [48,  
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38 49]. The BC-CNT-NZ's capacitive response at the lowest frequency of 20 mHz is 65 mF. This value was  
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40 evaluated by the Eq.5:  
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$$45 \quad C = 1 / Z_i 2\pi f \quad (5)$$

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49 Where  $Z_i$  is the imaginary component of the impedance at the frequency  $f$ . On the other hand, for GDE, the  
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51 capacitive response evaluated at 20 mHz by eq. 5 is 733  $\mu$ F. Therefore, EIS showed that both resistance  
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53 and capacitance of BC-CNT-NZ electrodes are better than GDE.  
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#### 57 **3.4.2. LSV and CV tests**

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4 The LSV reported in Fig.6 A indicates that for BC-CNT-NZ the ORR onset potential is at least 100 mV  
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6 higher than GDE. This is beneficial to achieve a high SCMFC voltage operation. Additionally, the cellulosic  
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8 cathode produced much more current over the voltage range investigated. At -0.3 V vs Ag/AgCl, a current  
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10 of 0.75 mA was achieved. Furthermore, the slope of linear part of the LSV was higher for BC-CNT-NZ, in  
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12 agreement with its lower impedance evaluated by EIS. These findings indicate that BC-CNT-NZ can be a  
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14 suitable air-cathode that features higher catalytic activity than GDL. The purpose of CV analysis was the  
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16 evaluation of the capacitive performance of the electrodes (Fig.6 B).The voltammetric currents of BC-CNT-  
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18 NZ's are dramatically higher than those of the GDE, therefore indicating a higher capacitance of the former  
19  
20 electrode with respect to the latter. Indeed, the capacitance resulted of 84.44 mF and 2.47 mF for BC-CNT-  
21  
22 NZ and GDL, respectively. Therefore, CNT is effective in providing to BC both the suitable electrical  
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24 conductivity for current collection and also acceptable capacitive behaviour. Thus, LSV and CV gave  
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26 indications about the catalytic activity and capacitive properties of BC-CNT-NZ.  
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### 3.4.3. Power density and polarization tests

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35 Fig.6 C report the LSV polarization (V-I) and power (P-I) curves of SCMFC assembled with BC-CNT-NZ  
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37 and GDL cathodes. The SCMFC could produce a maximum power density of about 80 mW/m<sup>2</sup> in presence  
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39 of BC-CNT-NZ that was three times higher than the power delivered by the cell with the GDE cathode (25  
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41 mW/m<sup>2</sup>). The OCVs were almost the same for the two cells. However, the initial voltage drop at the lowest  
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43 currents of the SCMFC with the GDE was much higher than BC-CNT-NZ. Also the slope of the linear part  
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45 of the polarization curve at the middle-high currents was lower. These two features are in agreement with  
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47 the higher resistance and lower capacitance of the GDE vs. the BC-CNT-NZ cathode. To make this  
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49 improvement more clear, single electrode potentials were monitored during the polarization tests, and the  
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51 results are reported in Fig.6 D. The anode behaviour was similar for the two cells, but the GDL cathode  
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53 showed higher voltage drop at the lowest currents and higher slope at the middle-high currents with respect  
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55 to the BC-CNT-NZ. This indicates the overall SCMFC response is mainly affected by the cathode  
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57 performance and it is improved by the substitution of GDL with BC-CNT-NZ. In this work, it was a  
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4 noteworthy point that making a homogenous junction between BC and CNT resulted in a minimum ohmic  
5 drop in MFC. Previously maximum power density of 2.42 mW.m<sup>-2</sup> was reported by using treated BC as a  
6 membrane for conventional carbon cloth based GDE [25]. The low power may be attributed to poor  
7 connection of BC to GDE. Hence, our results demonstrate that by our approach we succeeded in producing  
8 an effective BC based, monolithic MEA air cathode. The CNT layer exposed to air (Fig. S1) provided a  
9 good access to oxygen and showed interesting ORR electrocatalytic response. In parallel, the NZ coating  
10 exposed to the anolyte played the role of membrane and separator preventing leakage by a well-balanced  
11 wettability and hydrophobicity. Moreover, durability of binder-less CNT coating was already demonstrated  
12 in previous reports [24, 32]. In this work, after more than two months, the coating was not defected and did  
13 not release.  
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#### 26 27 **3.4.4. RDE experiments**

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29 To get insight into ORR electrocatalytic activity of BC-CNT-NZ, CNT modified glassy carbon (GC) and  
30 bare GC electrodes were studied by RDE in oxygen saturated buffer solution. Fig. 7 A shows the RDE  
31 LSVs at 5 mV/s and 0, 400, 900, 1600 and 2500 rpm. The CNT-GC RDE current density is a combination  
32 of capacitive and faradic components. The LSV curves were analysed to give the K-L plots (reported in  
33 Fig. 7 B) in a potential range where the response is affected both by kinetic and mass transfer limitations.  
34 In order to eliminate the contribution of the capacitive currents, at each potential the LSV current density  
35 was subtracted by the value measured in Ar-saturated solution. The slope of the K-L plots ( $\beta$ ) (Eq. 2)  
36 depends on the number of electron transferred in the ORR process [35]. Higher slope corresponds to a lower  
37 number of electrons. The K-L slope for CNT-GC is 1.84 and lower than that obtained with bare GC (Fig.  
38 S2, 3.56). This indicates that CNT could increase the number of electron transferred in ORR with respect  
39 to GC. Furthermore, the slope of Tafel plot (inset of Fig. 7 A) for CNT-GC was 6.15 and lower than that of  
40 GC (10.91). All the data for bare GC electrode is visible in Supplementary file Fig. S2 A & B.  
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#### 58 **3.4.5. GLV discharge tests**

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4 Fig.8 reports the power delivered by the SCMFC evaluated by GLV discharges with pulse time of 0.1, 0.5,  
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6 1 and 2 s. This kind of power curve can show brightly the potential application of MFC as a power supply  
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8 for an electronic consumer. The highest pulse power values of 800, 1030, 1210 and 1790 mW/m<sup>2</sup> can be  
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10 achieved at currents of 1.6, 2.2, 2.8 and 4 mA for the MFC with BC-CNT-NZ cathode. This cell delivers  
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12 around two fold higher power than that of the cell with the GDE. Also, it was shown that by decreasing  
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14 pulse time, the generated power was further boosted.  
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### 18 **3.5. BC-CNT-NZ as a monolithic MEA versus cellulosic membrane and air-cathodes: performance** 19 20 **and properties in MFC** 21 22

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24 Table 2 provides details of using cellulose in fabricating membrane and air-cathodes in MFCs. Biffinger et  
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26 al. used cellulose nitrate at a mini DCMFC with graphite felt as anode and cathode. In the work cellulosic  
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28 membrane showed lower power density (40 mW.m<sup>-2</sup>) than that by Nafion [50]. In other work, BC was  
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30 utilized in a huge DCMFC as proton exchange membrane with carbon plate electrodes. The system could  
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32 increase power density more than two folds rather than that by commercial cation exchange membrane.it  
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34 showed high potential of bacterial cellulose as a cheap alternative to expensive Nafion [51]. Ci et al. treated  
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36 cellulose by esterification and then used it in behalf of PTFE hydrophobic layer on carbon cloth air cathode.  
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38 They could improve MFC performance by the substitution and also decrease the cost of air-cathode by  
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40 elimination of PTFE. Although, they used platinum as catalyst which is not economical for MFC  
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42 technology[11]. Also, cellulose was not applied as membrane in the work. In other research, Wang et al.  
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44 put a mixed cellulose ester membrane between platinum catalyst layer on GDE and anolyte. The separator  
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46 layer's performance was similar to Nafion's[52]. In 2017, Marzorati et al. used the cellulosic shell of Maize  
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48 stalks as separator in a cylindrical SCMFC on commercial GDE-carbon black and reached power density  
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50 of 44 mW.m<sup>-2</sup> [53]. In the work diameter of Maize stalk was limiting factor for MFC size. More recently,  
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52 Vilela et al. in 2019 synthesized Poly (4-styrene sulfonic acid) treated BC as a separator in a SCMFC which  
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54 produced 2.42 mW.m<sup>-2</sup> with platinum coated GDE[54]. All aforementioned GDEs were fabricated by high  
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56 cost PTFE as hydrophobic agent and Nafion or PTFE as binder for catalyst coating. Also, the cellulosic  
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4 membranes as separators were apart from GDEs and there was not homogeneous contact between  
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6 membranes and GDEs unlike the monolithic MEA in this work. It should be noted that for a fair comparison  
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8 of the mentioned cellulose based MFCs' performance, it is necessary to consider power measurement  
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10 method. Resistance loading, LSV and galvanostatic discharge are different methods for measuring output  
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12 power of MFC. Reported output power may differ because of different values of parameters such as: scan  
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14 rate, resistance values, discharge current and pulse time. For example Ci et al. used resistance loading and  
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16 did not mention pulse time of each loading, while Vilela et al. used discharge test with pulse currents of 5  
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18  $\mu\text{A}$  and pulse time of 3 minutes. It may be the reason of considerable differences between the power density  
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20 values in Table 2. In this work, in order to report power density, LSV test and GLV discharge gave rise  
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22 maximum power densities of  $80 \text{ mW.m}^{-2}$  and  $1790 \text{ mW.m}^{-2}$  respectively which is higher than that of  
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24 previous reports. Other improvement in this work by fabricating a homogenous and monolithic BC based  
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26 MEA, was eliminating both carbon cloth and PTFE which means decreasing the cost of MFC. Cheap NZ  
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28 was used for the first time for cellulose hydrophobization by a very easy method of coating, CNT was  
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30 coated as both conductive carbon and catalyst instead of high cost platinum by a binder-less method. This  
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32 monolithic MEA could prevent anolyte leakage. In addition to explained DO experiment, by a simple  
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34 electrochemical test it was proved that the MEA is an excellent oxygen barrier. With reversing the face of  
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36 electrode (CNT face to anolyte side and NZ face to air) the open circuit voltage of cathode showed  
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38 downward trend and reached  $-0.37 \text{ V}$  after 20 days of MFC operation. It implied on non-availability of  
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40 oxygen in sludge. It was expected from BC as a nano-cellulose oxygen barrier. Thus, BC-NZ demonstrated  
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42 an excellent role as oxygen barrier to prepare anaerobic condition in anolyte of MFC.  
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#### 49 50 **4. Conclusions**

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53 To the best of our knowledge, a monolithic MEA based on hydrophobic BC was fabricated for the first time  
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55 and it was used as MFC's air-cathode. Very simple coating method was exploited for hydrophobization of  
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57 BC by the cheap NZ for the first time. NZ coating made a balance between hydrophobicity and wettability  
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59 of BC. Afterward, the electrode performance as an air-cathode was compared with a commercial GDE with  
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4 PTFE based hydrophobic layer in a SCMFC. EIS showed much lower impedance of BC-CNT-NZ rather  
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6 than GDE. Also, LSV and CV in agreement with EIS, showed higher catalytic activity and much higher  
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8 capacitive behaviour of cellulosic cathode. In LSV test, BC-CNT-NZ boosted power density by 320% in  
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10 comparison with that of commercial PTFE-carbon cloth GDE. It is the best performance of a cellulosic  
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12 MEA ever achieved at MFC. Thus, using cheap NZ for hydrophobization of BC showed it is an excellent  
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14 alternative to PTFE.  
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4 **Figure captions:**  
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8 **Fig. 1 (A)** Fabrication procedure of MEA air-cathode based on BC, CNT and NZ and **(B)** SCMFC configuration in  
9 this work.  
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12 **Fig. 2 (A)** ATR-FTIR spectra of BC and BC-NZ, **(B)** EDX mapping and surface atomic distribution of  
13 BC-NZ, **(C)** XRD spectra and **(D)** Thermal stability behaviour of BC and BC-NZ.  
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18 **Fig. 3** FESEM image and WCA of bare BC **(A)** and BC-NZ **(B)**, AFM image of bare BC **(C)** and BC-NZ **(D)**.  
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21 **Fig. 4 (A)** The role of BC-CNT-NZ in SMFC and the effect of WCA on MEA's performance, **(B)** DO and **(C)**  
22 Evaporation rate versus time.  
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26 **Fig. 5** Nyquist plot of BC-CNT-NZ and GDE in frequency range of 100 KHz to 20 mHz.  
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29 **Fig. 6** LSV **(A)**, CV **(B)** of BC-CNT-NZ and GDE at 10 mV/s in sludge, Power density and polarization of the  
30 SCMFC cells **(C)** and Polarization test of single electrodes **(D)**.  
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34 **Fig. 7 (A)** LSV at 5 mV/s and different rpm of CNT-GC RDE and corresponding Tafel and **(B)** K-L plot.  
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37 **Fig. 8** Pulse power density of the SCMFC cells evaluated by GLV discharges with pulse time of: 2 s **(A)**, 1 s **(B)**, 0.5  
38 s **(C)** and 0.1 s **(D)**.  
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41 **Captions of tables:**  
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44 **Table 1** Total crystalline index, lateral order index and hydrogen bond index of BC and BC-NZ  
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47 **Table 2** Application of cellulosic materials in membrane and air-cathode of MFCs  
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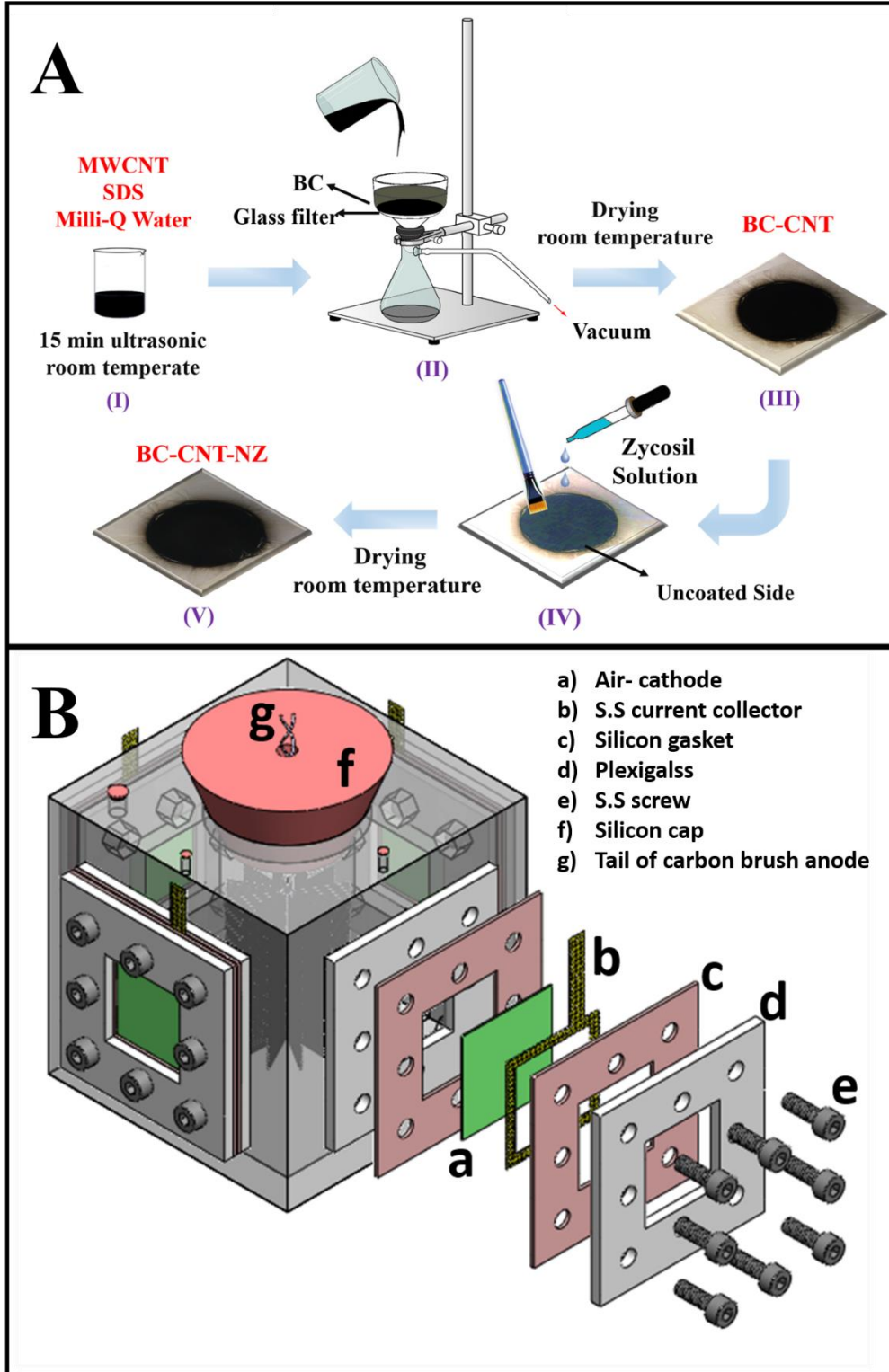


Fig.1

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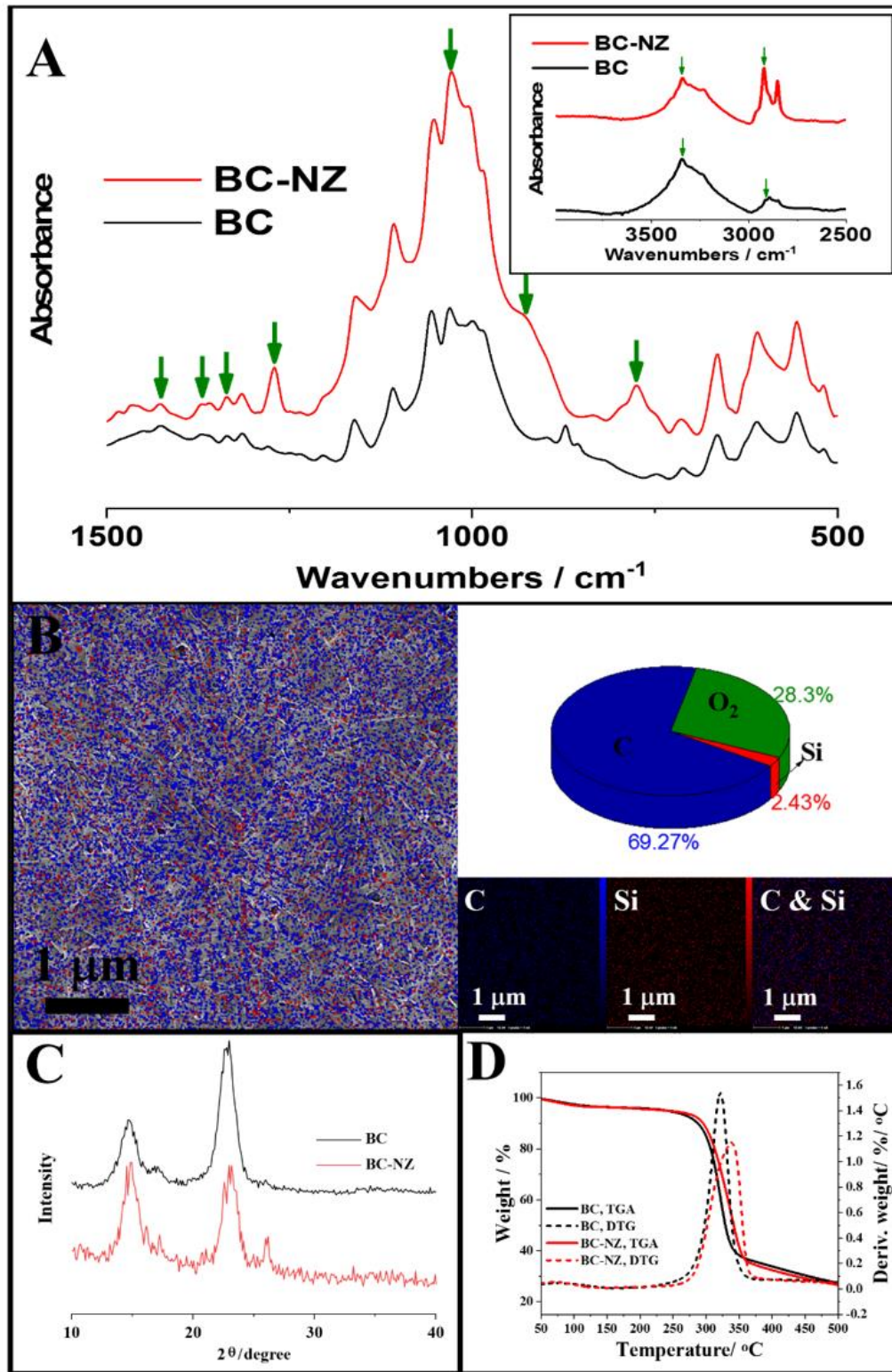


Fig. 2



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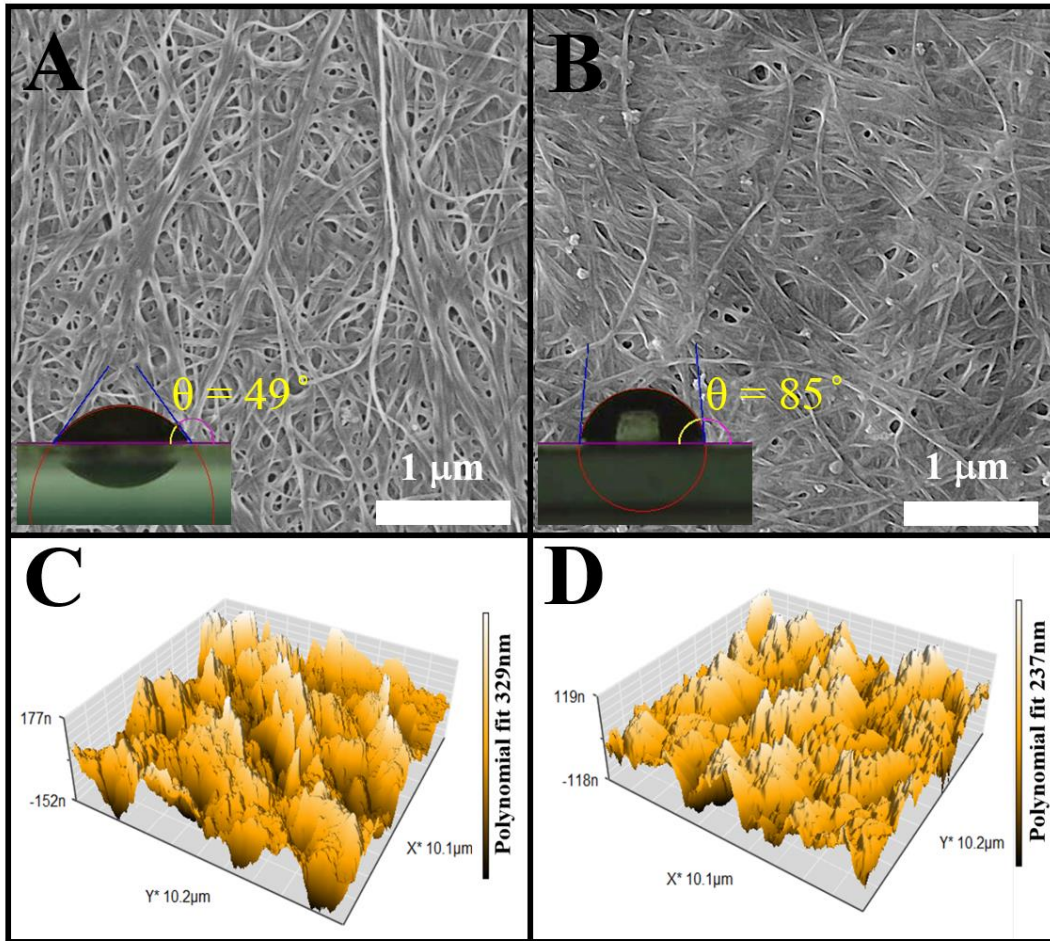


Fig. 3



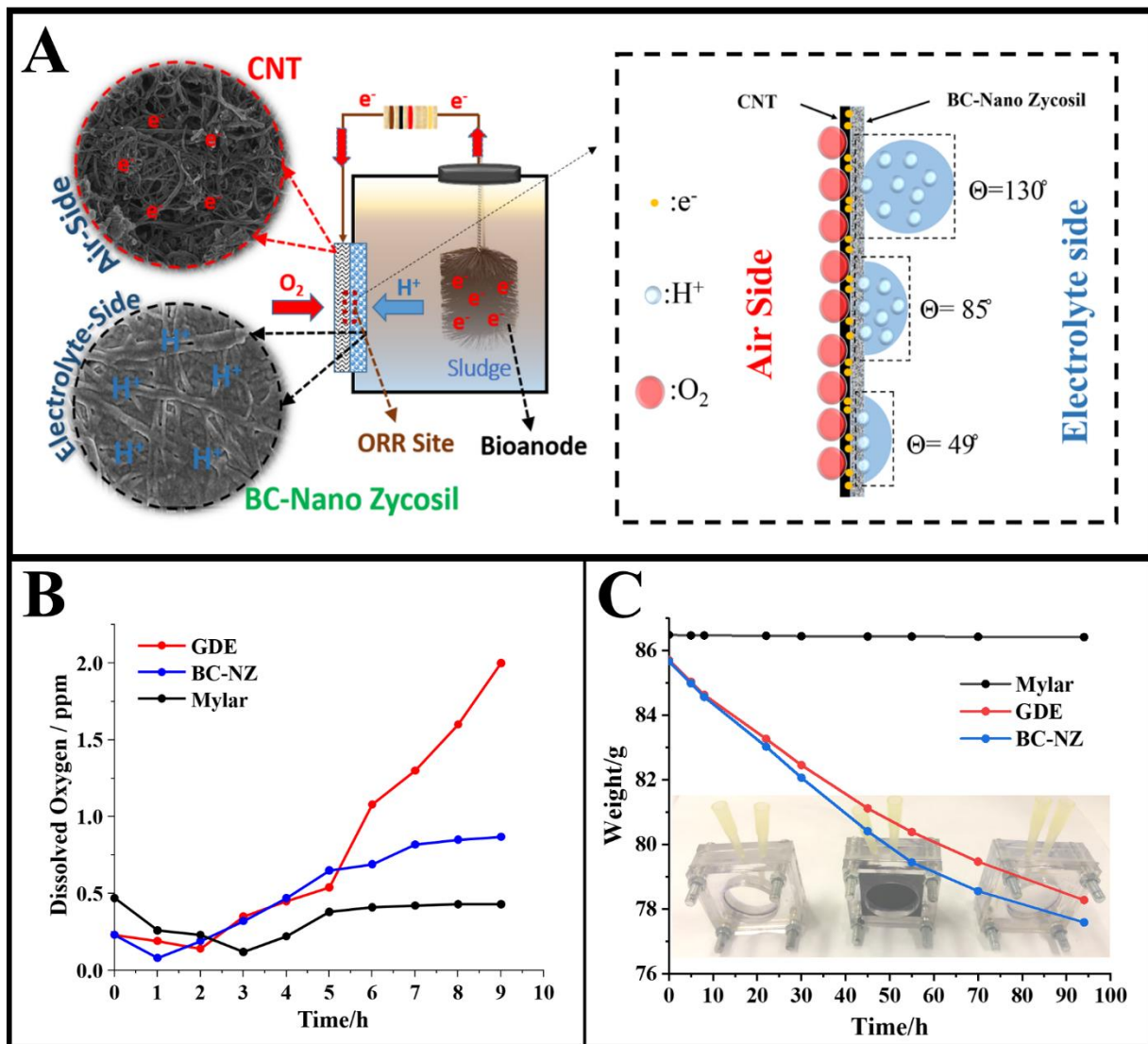


Fig. 4

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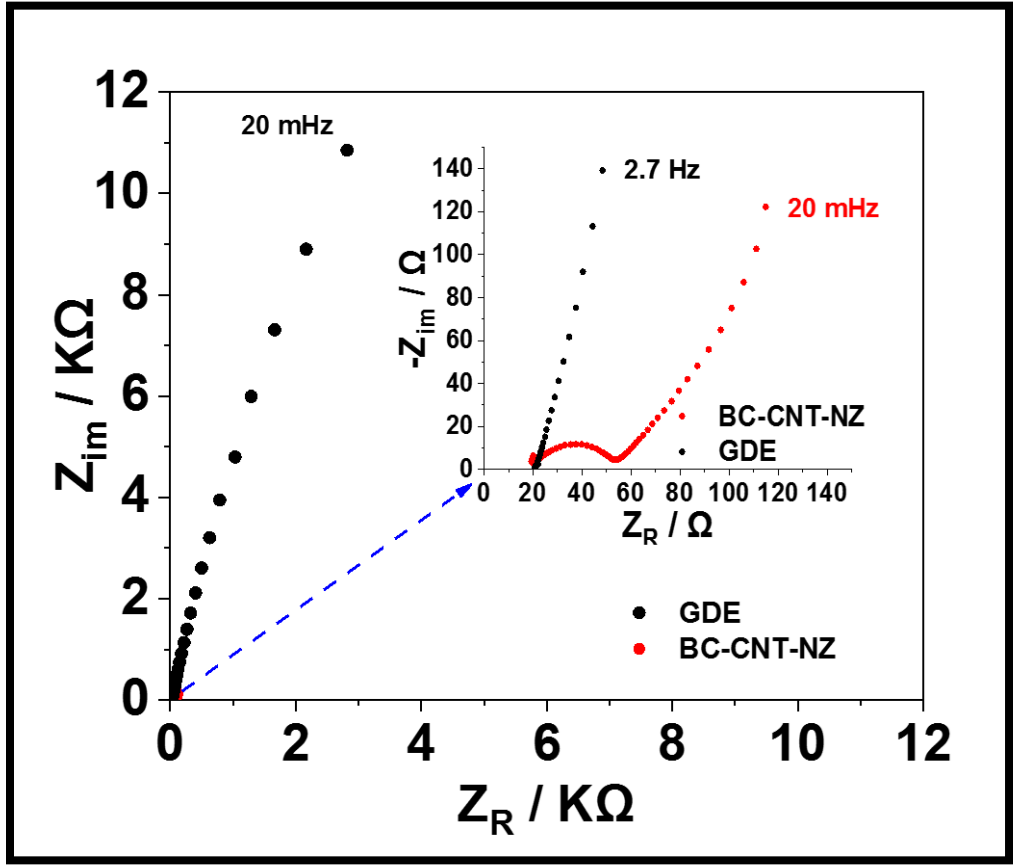


Fig. 5

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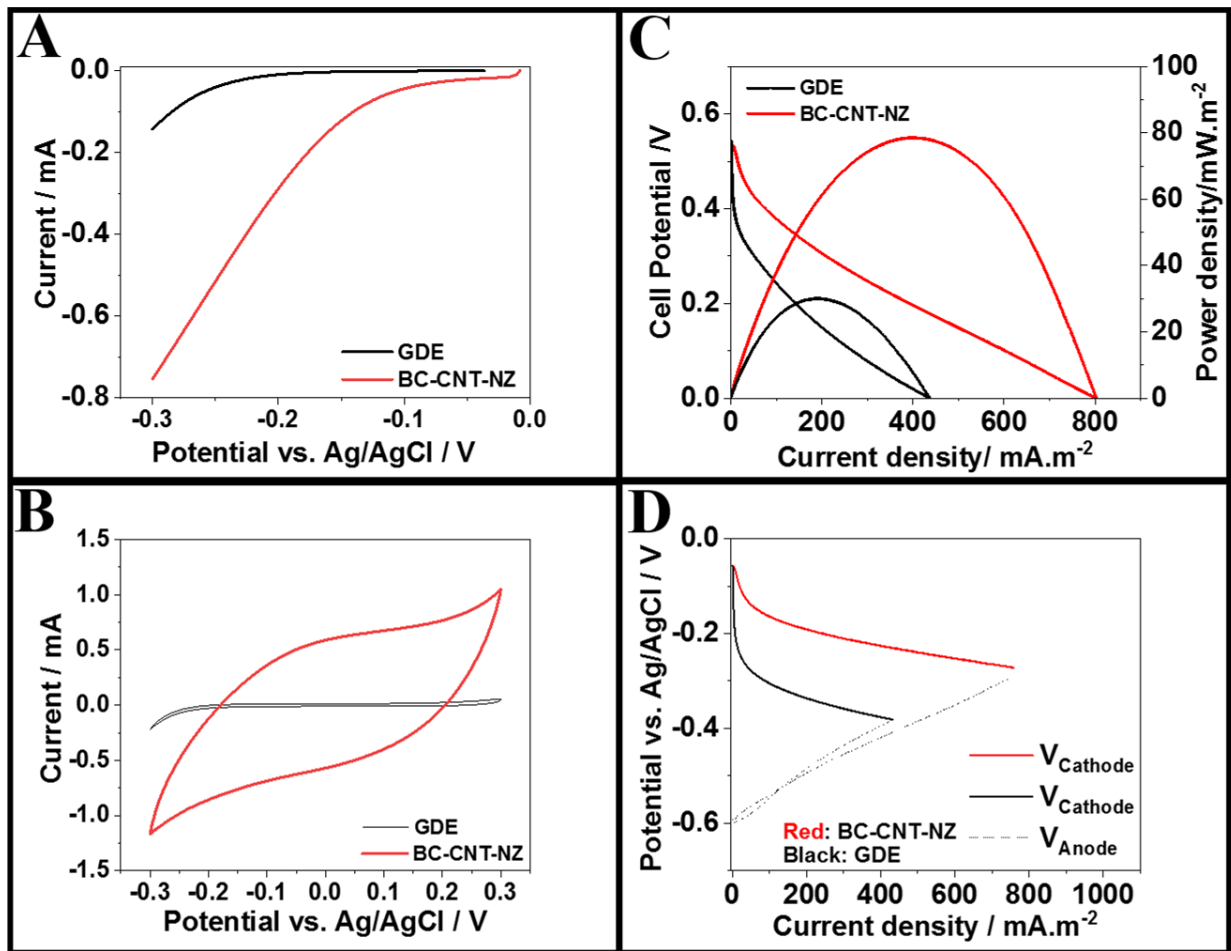


Fig. 6

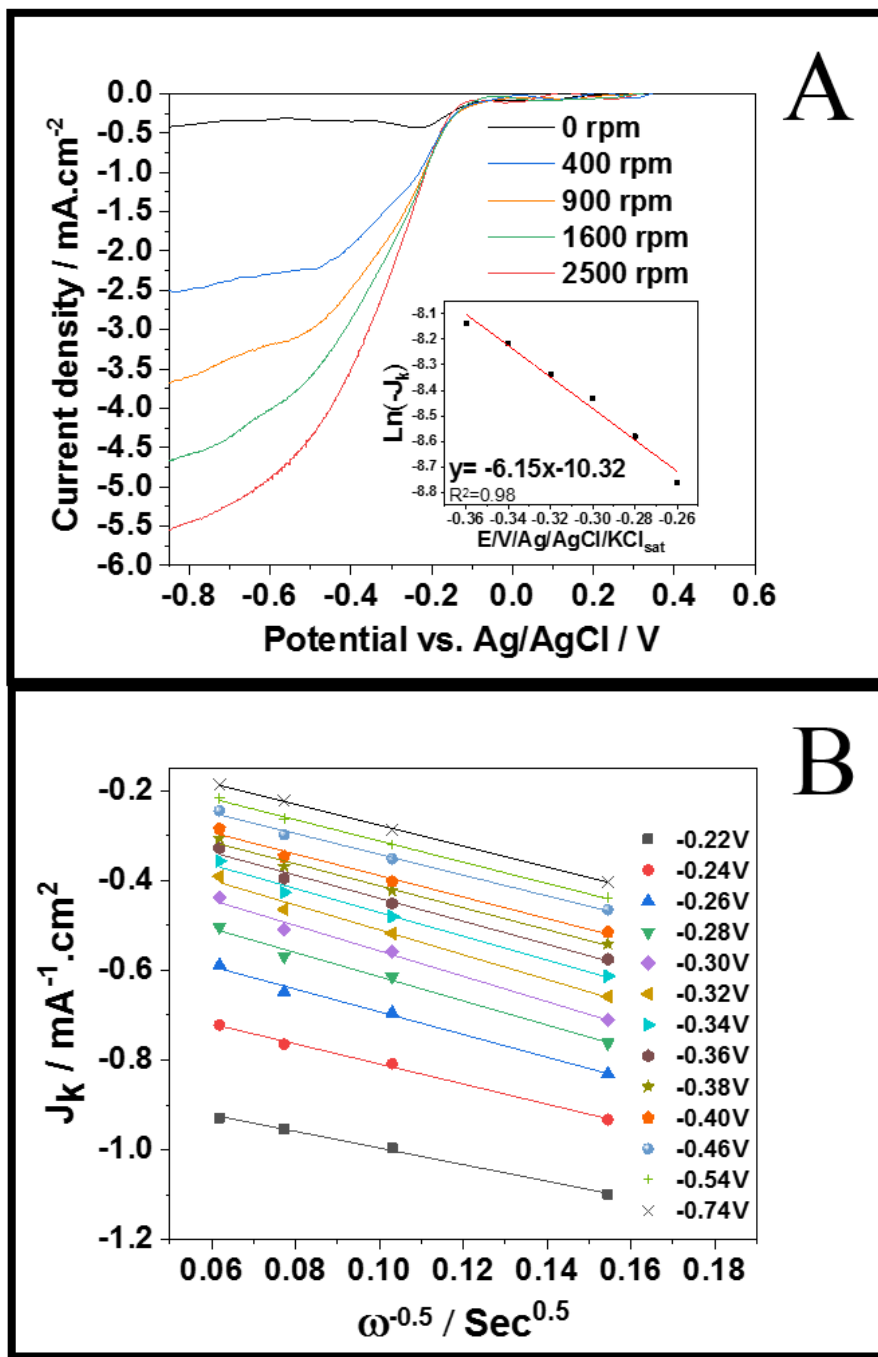


Fig. 7

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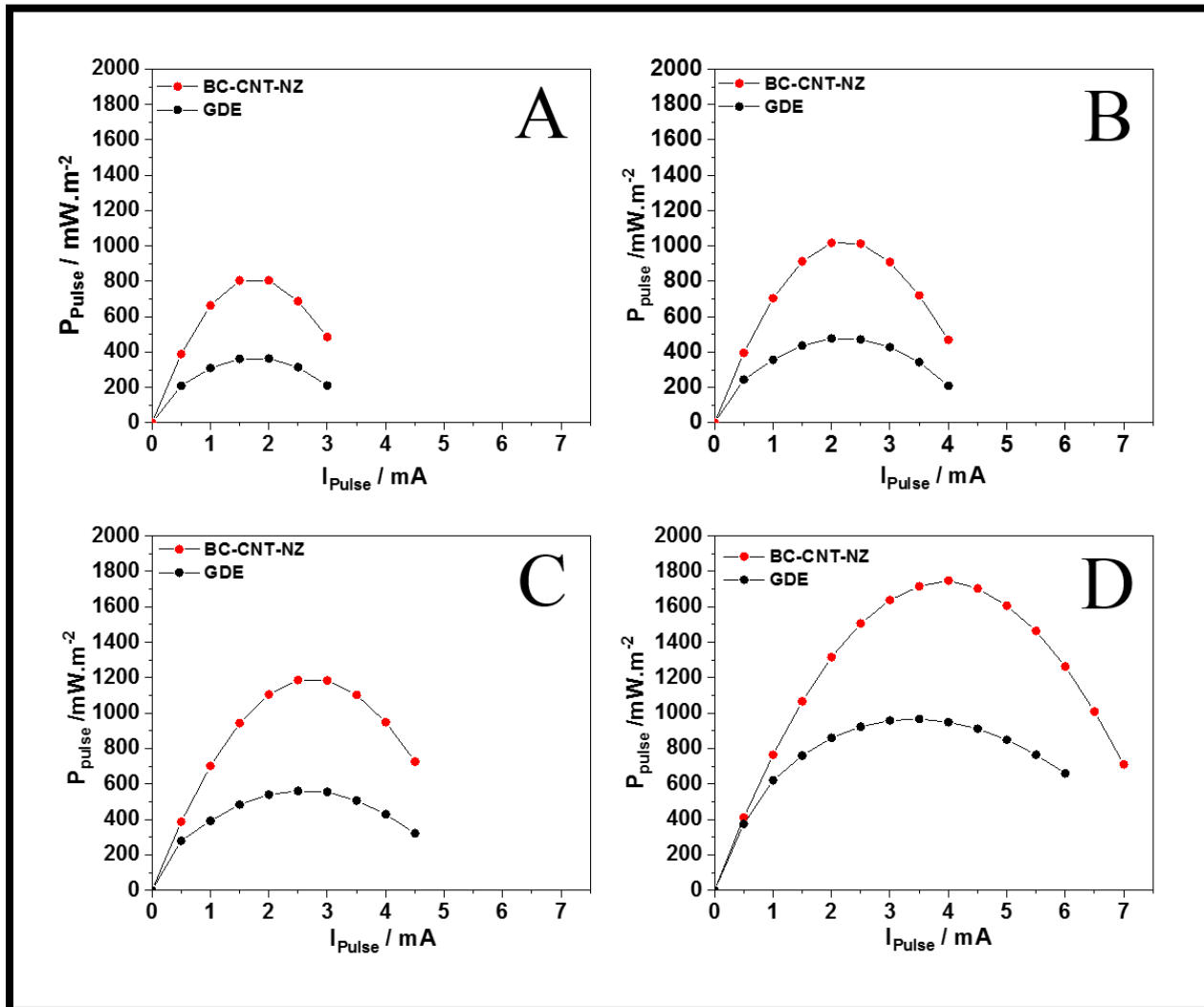


Fig. 8

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**Table 1**

	<b>TCI</b>	<b>LOI</b>	<b>HBI</b>
<b>BC</b>	1.04	1.02	1.01
<b>BC-NZ</b>	0.97	0.85	1.01

Table 2

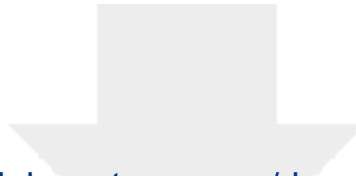
Cellulose membrane	Anode	Cathode	Configuration	Hydrophobic layer	Binder	Volume	Bacteria	Power density	Ref
Cellulose nitrate	graphite felt	Graphite felt	DCMFC	-	-	1.2 ml	<i>Shewanella oneidensis</i>	40 mW/m <sup>2</sup>	[50]
BC	Carbon plate	Carbon plate	DCMFC	-	-	45 lit	Soil (mixed culture)	73-200 mW/m <sup>2</sup>	[51]
-	Carbon felt	Carbon cloth-cellulosic GDL with platinum	SCMFC	Esterified cellulose nano fiber	Nafion	27 ml	Mixed culture	1518.3 mW/m <sup>2</sup>	[11]
Mixed cellulose ester filter	Carbon brush	Commercial GDE with platinum 0.5 mg/cm <sup>2</sup>	SCMFC	PTFE	-	250 ml	Anaerobic sludge	780.7 mW/m <sup>2</sup>	[52]
Giant canes and Maize stalks cellulose	Carbon cloth	Carbon cloth GDE with carbon black	SCMFC	PTFE	PTFE	-	Swine manure of a pig-farm	44 mW/m <sup>2</sup>	[53]
Poly(4-styrene sulfonic acid)/BC	Carbon brush	Carbon cloth GDE with platinum 0.1 mg/cm <sup>2</sup>	SCMFC	PTFE	-	900 ml	<i>Shewanella frigidimarina</i>	2.42 mW/m <sup>2</sup>	[54]
BC based MEA	Carbon brush	BC-CNT	SCMFC	NZ	Binderless	250 ml	Mixed culture	80-1790 mW/m <sup>2</sup>	This work

**Declaration of interests**

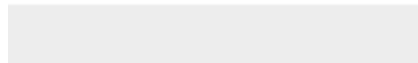
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:





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