

Improving the performances of NafionTM-based membranes for Microbial Fuel Cells with silica-based, organically-functionalized mesostructured fillers

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Abstract

Microbial Fuel Cells (MFCs) can be conveniently used for wastewater treatment and bioelectricity production. Their efficiency is strongly influenced by the physico-chemical properties of the ion-conducting membrane. In this work we prepare NafionTM-based composite membranes by using mesoscale SBA-15 silica, and organic-inorganic fillers obtained by functionalizing SBA-15 with SO₃H groups. The proposed membranes are tested as alternative separators in MFCs for applications in wastewater treatment and their performances compared to those of standard NafionTM 117. Prolonged (3 months) MFC operation show that the composite membrane with 5 wt% of SBA-15 functionalized with 10 mol% of SO₃H gives maximum power density of 380 mW m⁻³, namely three times better than that of NafionTM after 90 days of operation. The same membrane offers a very effective COD removal after 14 days (more than 95%), an impressive coulombic efficiency of 34%, and very high resistance to biofouling. We conclude that the use of silica-based SO₃H functionalized fillers is a powerful strategy to improve the performances of NafionTM membranes in MFCs.

KEYWORDS: Microbial Fuel Cells; MFC; Nafion; Composite Membranes; PEMs; wastewater treatment

1. Introduction

Bioenergy is an emerging economy field, which is expected to play a fundamental role in the expansion of the non-fossil-fuel technologies to tackle the global warming, and to make more sustainable the increasing energetic requirements of the modern society. It is renewable energy made available from materials derived from biological sources (biomasses), which can be converted into bioalcohols, biodiesel, biohydrogen, and also directly into bioelectricity [1].

One of the most promising bioenergy technologies is based on the concept of microbial fuel cell (MFC), namely a bioreactor able to convert the chemical energy of different organic and inorganic substrates into electric power through catalytic reactions promoted by microorganisms [1-3]. MFCs are intensively investigated for wastewater treatment, and in general for water management. In fact, MFCs play a dual advantageous role: i) they can use wastewater streams, otherwise not utilized, to produce bioelectricity; ii) at the same time, they treat the wastes, by degrading the organic substrate, and give purified water.

A huge number of publications and reviews on MFCs were recently reported in literature, which assessed methods and terminology, electrochemical mechanisms, techniques for the analysis of the performances, device assemblies, substrates, microbiology and actual sustainability [2-6]. Consequently, several advances on the MFC technology were obtained during these last years. In particular, an enhancement of five magnitude orders in the cell maximum power density was reached by continuously optimizing the cell configuration as well as electrodes and electrolyte materials [3].

The MFC basic cell setup consists of a dual-chamber (H-type cell) composed by anode and cathode compartments, separated by a proton exchange membrane (PEM). At the anode, a bacteria biofilm oxidizes the substrate (generally organic in case of wastewater), with production of electrons, protons and other more complex cations. Electrons migrate through the external circuit towards the cathode compartment, where the oxygen reduction reaction (ORR) takes place. Protons, in contrast, migrate across the membrane to react with oxygen to produce water. A more simplified MFC configuration consists of an anode chamber and an open-to-air electrode, where the cathode layer is directly assembled with the separator. Single-chamber MFCs are frequently used also in the membrane-less configuration [2].

Despite of the numerous technological advantages provided by such devices, some drawbacks still limit their industrial exploitation, in particular high production cost and low attainable power density. Regarding the power issue, important improvements were obtained by moving towards other cell architectures, as for instance tubular, plane and stacked MFCs, but also by developing new materials for electrodes and separator [3].

Such a rapid development, and the increasing worldwide attention, made it essential the effort to classify the existing devices, and to establish terminology, benchmarking, and analysis methodologies of the functional properties [3, 4, 7].

The membrane separator is probably the most important factor affecting the performances and the cost of the MFC. In particular, it plays a key role in cell internal resistance, biofouling, oxygen diffusion, substrate loss across the membrane, and pH change [8, 9]. The common membranes used as separators for MFCs are grouped into four main classes: cation exchange membranes (CEM), proton exchange membranes (PEM), anion exchange membranes (AEM), polymer-composite membranes and porous systems [8, 10].

Proton exchange membranes are indeed the most frequently used [9]. Within a wide spectrum of proposed materials, NafionTM still remains the most representative separator, due to its high proton conductivity, low membrane resistance, chemical and thermal stability. Among the numerous types tested as ion exchange membrane, NafionTM 117 seems to be the best compromise of several properties. Even if the reported maximum voltage and power densities (668 mV and $\sim 10 \text{ mW m}^{-2}$, respectively) are lower than those obtained in presence of thinner membranes, as for instance NafionTM 112, it shows higher oxygen and substrate permeability [8]. The major drawbacks of NafionTM-based MFCs are concerned with oxygen leakage from cathode to anode, substrate loss, transport and accumulation of cations different from protons, biofouling [11, 12] and, last but not least, high cost that may contribute more than 35% to the total cost of the device [8].

One technological approach to manage most of these issues is dispersing inorganic fillers into NafionTM, to prepare composite membranes as separators for MFCs. Contrary to the chemical fuel cells, where the beneficial use of NafionTM-based composites is well established [13], the role of inorganic particles on the bioelectrochemistry of MFCs has not yet been fully explored. Few examples are available in literature, which prove that proper additives seem to have beneficial effects on proton transport, and on the enhancement of the cell maximum power density and coulombic efficiency. In particular, zeolites, sulphonated TiO₂, nano-Al₂O₃, hybrid organic-inorganic fillers as Zirfon[®] and Fe₃O₄ particles were

recently dispersed into Nafion™, Nafion™-like polymers and PEEK, to obtain composite separators for MFCs with improved properties [8, 14-17 and references herein indicated].

The present study describes the functional performances of three composites based on Nafion™ 117 and mesoporous silica (SBA-15), pure and functionalized with different amounts of propylsulfonic groups, as novel ion exchange membranes in a single-chamber MFC for the treatment of urban wastewater. The results are compared to those obtained in the benchmark case of a MFC using Nafion™ 117 as the separator. The work aims to validate the use of properly designed fillers in the development of novel PEMs as optimized and innovative separators for bioelectrochemical systems.

2. Experimental details

2.1 MFC Assembly

2.1.1 Preparation of the Nafion/SBA15 composites membranes

Nafion™ 117 (20 wt% in ethanol, Aldrich) was used as the starting polymer for the preparation of the membranes, both pure and composites. The chosen fillers were mesoporous silica (SBA-15) and SBA-15 functionalized with different contents of propylsulphonic groups (10 mol%: SBA-SO₃H10, and 50 mol%: SBA-SO₃H50). In particular, four types of materials were used as separators for the MFC assembly: pure Nafion™, Nafion™/SBA-15, Nafion™/SBA-SO₃H10 and Nafion™/SBA-SO₃H50. The filler amount was 5 wt% with respect to the polymer. The SBA-15 based fillers were synthesized by sol-gel template route, as reported elsewhere [17].

All the membranes were prepared by spraying method, as reported in more details in a recent paper [18]. In particular, 16 cm² films of Nafion™ and composites were obtained by spraying a proper volume of the polymer starting solution, obtained by mixing 1 mL of a 20% w/w Nafion solution in water/ethanol and 9 mL of ethanol, with an aerograph on a plate heated at 70°C under N₂ flow in a ventilated chamber. In case of composite systems, the filler (15 mg) was first dispersed in the starting solution, which was subsequently sonicated for about 30 minutes. The films were peeled out in distilled water and then activated by the following subsequent steps before use: i) immersion in a boiling H₂O₂ solution (3 wt%) for 2 hours, ii) washing in distilled water for 1 hour, iii) immersion in a boiling solution of H₂SO₄ 0.5 M for 1 hour, and finally washing three times in distilled water for 15 min. The resulting

membranes, both pure and composite, were ~60 μm -thick with a thickness uniformity of about 99%.

2.1.2 Preparation of the electrodes and cell configuration

Single chamber MFCs were assembled by using NafionTM and NafionTM-based composites as PEMs, Pt-C (40%) on carbon cloth as air cathode and pure carbon paper as anode. In particular, the open-to-air cathode was fabricated by spraying a dispersion of platinum and carbon black onto a gas diffusion layer (SGL carbon – Sigracet 34bc). The ink was composed by 22.5 mg of Pt/C in 9 mL of ethanol, added to 0.15 ml of the starting ionomer solution (NafionTM in ethanol, 20%). The anode was plain SGL carbon paper.

The membrane and the cathode layers were assembled by hot pressing at 80°C under 1 ton for 10 minutes. The anode-projected area was 56 cm² (both sides of the electrode) whereas the cathode-projected surface was 8 cm² in case of MFCs based on NafionTM and NafionTM/SBA-15, and 4 cm² for the cells mounting composites with sulphonated SBA-15 silica.

The two compartments were assembled in a 100 mL glass bottle with a working volume of 75 mL (see Figure 1) with the anode placed as close as possible (about 1 cm) to the membrane.

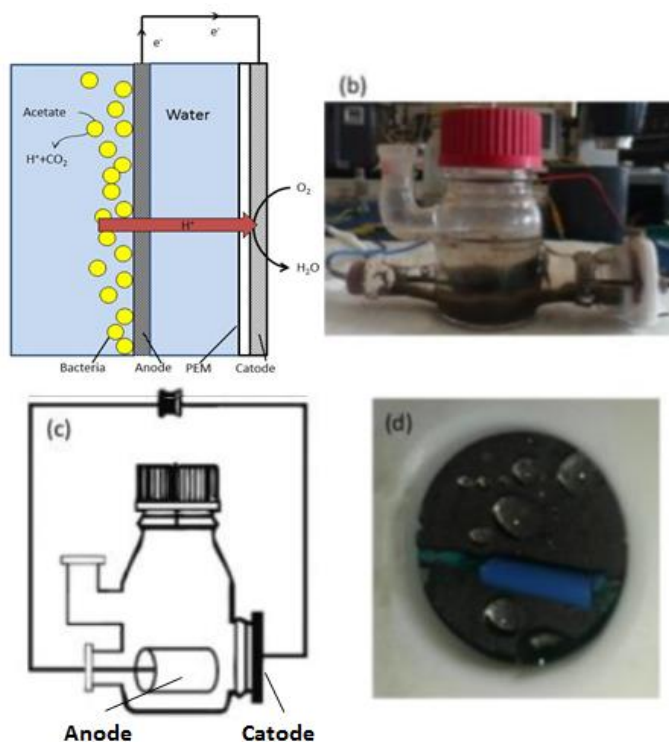


Fig.1: Scheme of the open-to-air MFC (a-c); water droplets formed at the cathode compartment (d).

All MFC reactors were operated at room temperature in a fed-batch mode in duplicate, after inoculation performed by using returned sludge taken from an activated sludge process (Milan Municipal Wastewater Treatment Plant, Italy). In order to have a better control on the original real waste-water and to avoid the growth of undesired microorganisms during the long-term experiments, the electro-active bacteria were fed with a 10 mM solution of CH_3COONa each week as the carbon source (namely 200 mg/week in the anodic chamber), whose COD was 2700 mg L^{-1} . A buffered nutrient solution (pH=7) consisting of KH_2PO_4 (5.8 g L^{-1}), K_2HPO_4 , (10.0 g L^{-1}), NH_4Cl (0.1 g L^{-1}) and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.01 g L^{-1}) was also added.

The cells were kept under an external load of 100 ohm before the measurements, which were always carried out at pH=7.

2.2 Measurements

The surface morphology of the membranes before and after the experiments was observed by using a scanning electron microscope (Zeiss MA10). The samples were previously gold-sputtered. The images were collected by deeply mapping the sample at different magnitudes.

The membrane proton conductivity was measured by means of impedance spectroscopy, connecting a frequency response analyser (FRA Solartron 1255) to an electrochemical interface (Solartron 1287). The membrane was fixed to a four-points BekkTech conductivity cell, connected to the test stand BekkTech 411 for the temperature control. The impedance scans were performed at 30°C and at 100% R.H. The impedance spectra were fitted with the ZView 3.0 software (Scribner Associates, Inc.).

The electrochemical tests were performed throughout the whole experimental period (2000 hours). In particular, the overall polarization curves were collected at room temperature by means of an electrochemical interface (Solartron 1287) scanning the potential from Open Circuit Voltage (OCV) to 0 V, at 0.1 mV s^{-1} . The impedance spectra of the cells were collected over the frequency range 100 kHz-1 mHz at voltage amplitude of 100 mV.

COD measurements were carried out by means of HACH COD analyzer, using a ISO-15705 Kit.

The coulombic efficiency, ϵ_c , of the MFCs working in fed-batch mode was calculated over a period of time t and was determined by the following equation 1:

$$\epsilon_c = \frac{M \int_0^t I dt}{FbV_{an}\Delta_{COD}} \quad \text{eq.1}$$

where M is the molar mass of oxygen, F is the Faraday's constant, b is the number of electrons exchanged during the electrochemical reaction per mole of O_2 , V_{an} is the volume of the liquid in anode compartment and, finally, Δ_{COD} is the COD change over the time of the experiment [4].

The separator contact angle was measured by means of an optical contact angle/ surface tension meter (KSV CAM 200) depositing onto each swollen membrane a water drop of 5 μL .

3. Results and discussions

3.1 *The fillers of the composite membranes*

As already stated above, three NafionTM-based composite membranes were prepared and tested as novel ion exchange separators for single-chamber MFCs. These systems were compared to the unfilled NafionTM, working under similar experimental conditions, in order to investigate their functional performances and to address the role of the fillers on the bioelectrochemistry of MFCs.

The silica-based fillers differ for what concerns meso- and microstructure depending on the functionalization degree. Our previous characterization [19] via solid-state multinuclear NMR, TEM and XRD revealed that SBA-SO₃H10 totally retains the ordered mesoporous structure of SBA-15, despite of the organic functionalization. In this case, the sulfonic units are likely arranged inside the nanosize channels of the silica network. In contrast, SBA-SO₃H50 shows limited mesoporous domains inside a disordered network, where the higher number of SO₃H moieties is only partially distributed into the nanochannels.

3.2 Electrochemical properties of the single-chamber MFCs: polarization experiments and long-term performances

Table 1 summarizes the functional performances of all the investigated MFCs. In order to correctly address the actual role of the SBA-based fillers on the device bioelectrochemistry, similar conditions in terms of substrate and the fed-batch cycles were kept in all the studied systems. The pH and conductivity of the wastewater were 7.0 and 7.4 mS cm^{-1} , respectively.

Membrane	$\sigma_{30,m}$ (S cm^{-1})	P (μW)	PD_v (mW m^{-3})	PD_{an} (mW m^{-2})	PD_{cat} (mW m^{-2})	OCV (V)	$R_{(\Omega+m),s}$ (Ωcm^{-2})	$R_{(\Omega+m),f}$ (Ωcm^{-2})	R_p (Ωcm^{-2})	ϵ_c (%)	COD r.r. ($\text{mg dm}^{-3} \text{h}^{-1}$)	θ
Nafion TM	85	9	129	1.7	12	0.36	26	27	465	22	5.1	$96^\circ \pm 5^\circ$
Nafion TM /SBA-15	28	11	148	2.0	14	0.32	17	32	47	26	5.5	$93^\circ \pm 2^\circ$
Nafion TM /SBA-SO ₃ H10	62	28	380	5.0	75	0.75	58	73	75	34	6.7	$85^\circ \pm 4^\circ$
Nafion TM /SBA-SO ₃ H50	88	14	180	2.4	35	0.45	93	42	22	25	5.9	$70^\circ \pm 9^\circ$

Table 1: Separator Contact angles and Functional properties of MFCs based on Nafion membranes, working at room temperature with an external load of 100Ω , after 90 days of operation. $\sigma_{30,m}$: membrane proton conductivity @30°C and 100 % RH%; P : absolute power delivered by the cells; PD_v : Maximum Power Density to volume; PD_{an} : Maximum Power Density to anode; PD_{cat} : Maximum Power Density to cathode; $R_{(\Omega+m),s}$: Initial Cell Internal Resistance; $R_{(\Omega+m),f}$ and R_p : separated contributions to R_i (ohmic, membrane resistances and polarization resistance) after 90 days of operation; COD r.r.: COD removal rate; θ : contact angle measured on wet Nafion-based membranes.

Polarization experiments were performed on each cell throughout a test period of 90 days, by collecting curves each week. The plots were obtained by means of linear voltammetry using low scan rates (0.1 mV s^{-1}) in order to avoid overestimation of the power output. The resulting power densities were normalized with respect to the projected area of both cathode and anode and to the volume of the reactor [7]. Figures 2 and 3 report as an example the polarization data, normalized to the bioreactor volume, after 90 days of operation.

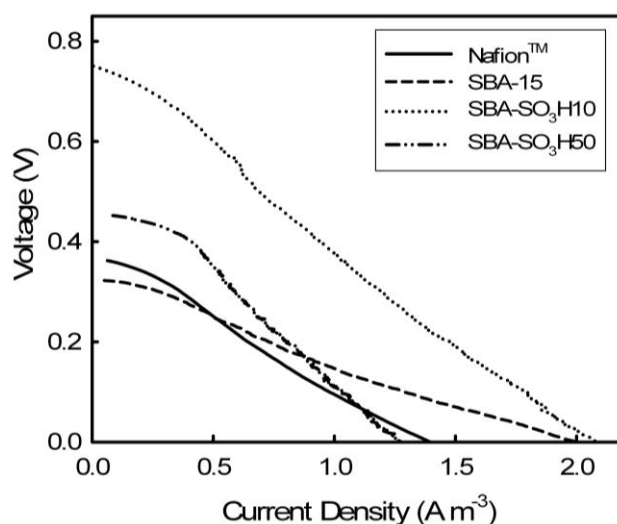


Fig.2: Polarization plots of the investigated MFCs based on different PEMs: unfilled NafionTM (solid line); NafionTM/SBA-15 (medium dashed line); NafionTM/SBA-SO₃H10 (dotted line); NafionTM/SBA-SO₃H50 (dash-dot lines).

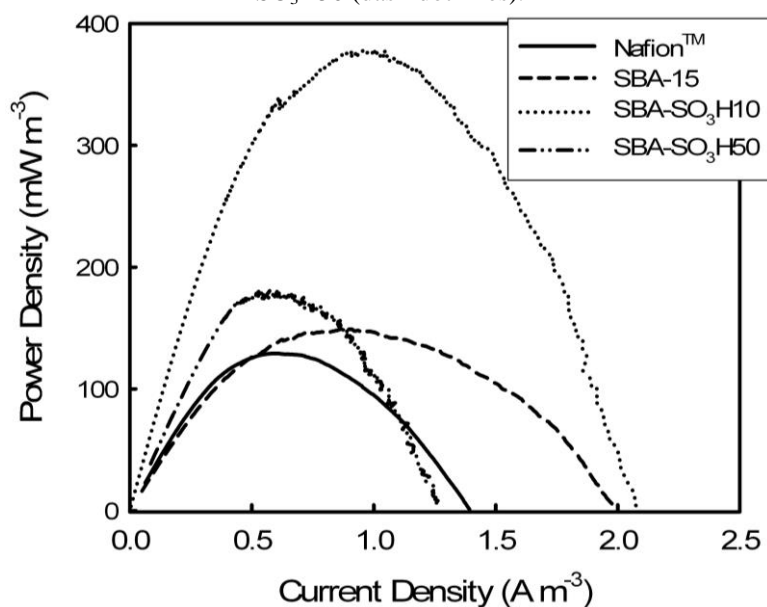


Fig.3: Power Density (normalized to the bioreactor volume) vs. Current Density after 90 days of operation of the investigated MFCs based on different PEMs: unfilled NafionTM (solid line); NafionTM/SBA-15 (medium dashed line); NafionTM/SBA-SO₃H10 (dotted line); NafionTM/SBA-SO₃H50 (dash-dot lines).

From the analysis of Table 1, we note that the dispersion of sulphonated SBA-15 in NafionTM remarkably improves the MFC performances with respect to the NafionTM/SBA-15 and even to the unfilled NafionTM. First of all, the presence of small amounts (5 wt%) of the organic-inorganic hybrid does not play a detrimental role on the membrane proton transport, as proved by the conductivity values. Contrary to the SBA-15 based composite, in case of sulphonated fillers the conductivity is quite similar to that of unfilled NafionTM, in particular for high content of SO₃H units (88 mS cm⁻¹@30°C). This is likely related to a higher water

adsorption and retention of the hybrid filler (compared to pure SBA-15), which facilitate the proton migration through the membrane.

Stable OCV values were reached after about 100 hours for all the MFCs. Higher OCVs are obtained in case of MFCs with sulfonated silica separators. In particular, OCV = 0.75V, which is very close to the highest cell voltage obtained so far [20], was obtained for the cell with the filler SBA-SO₃H10. The other values range between 0.32V and 0.45V, in agreement with the voltages generally reported in the literature, which are typically below 0.6V [4]. The factors decreasing the actual cell voltage with respect to electromotive force (e.m.f.) are well known and depend on several losses, namely activation, mass transport and also bacteria metabolism [4]. Differences in OCV could be also related to the microstructure and morphology of the membranes. The presence of the filler in the Nafion composites, for instance, may affect the microstructure and morphology of the separator, particularly in terms of porosity. For this reason, we may speculate that the system filled with SBA-SO₃H10 could be denser than the other membranes, with a consequent higher OCV.

As evidenced by Figures 2 and 3, the membrane NafionTM/SBA-SO₃H10 shows the best functional performances with the highest power output of 28 μ W and a corresponding maximum power density of 380 mW m⁻³. This value is roughly three times the power produced by a cell with standard NafionTM membrane as the separator. These values are also higher than those observed for the membrane filled with pure SBA-15, at least for current densities lower than 1 A m⁻³. Moreover, no voltage or power overshoot was observed. Overshoot phenomena concern the system response at high currents, where voltage and current drops may occur causing distortions in the polarization plots [7]. This phenomenon is generally interpreted in terms of dynamic adjustment of the microbial community to adapt to extreme current conditions [7, 21, 22]. The absence of overshooting in all the investigated cells indicates that a quite stable and mature biofilm was formed at the anode compartment during the anode-enrichment period and the fed-batch cycles.

In order to evaluate the membrane effect on the MFCs stability, long-term operation experiments were carried out for all the cells. Figure 4 reports the maximum power density, PD_{max}, obtained by the polarization data vs. the cell operation time. The time-dependent behavior of the cells reveals remarkable differences among the considered PEMs. First of all, the acclimation is achieved in different times. Most of the cells delivered the maximum power after 100 hours (namely unfilled NafionTM: 1623 mW m⁻³, NafionTM/SBA-SO₃H10: 1136 mW m⁻³ and NafionTM/SBA-SO₃H50: 970 mW m⁻³), contrary to that with NafionTM/SBA-15 for which the highest value (1235 mW m⁻³) was observed after 250 hours.

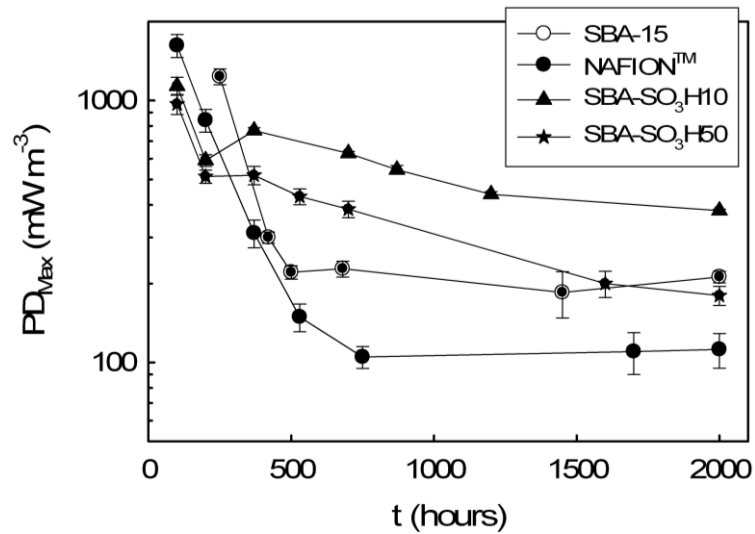


Fig.4: Time-dependent behavior of the Maximum Power Density for MFCs based on different PEMs: unfilled Nafion™ (open circles); Nafion™/SBA-15 (filled circles); Nafion™/SBA-SO₃H10 (triangles); Nafion™/SBA-SO₃H50 (stars). **The error bars are referred to the measurement standard deviations.**

The PD loss is smaller in case of cells based on composites with sulphonated SBA-15. After 90 days of operation, in fact, the power density for Nafion™/SBA-SO₃H10 underwent to a power drop of 66% (380 mW m⁻³), whereas more significant decreases were observed for the other systems, namely 81% (180 mW m⁻³) for Nafion™/SBA-SO₃H50, 83% for SBA-15 (148 mW m⁻³) and 93% for pure Nafion™ (to 129 mW m⁻³). Significant power drops with time were already observed in literature [see, for instance, ref. 22] and interpreted as due to a number biological, electrochemical and physico-chemical factors, including non-optimal applied load, precipitation of salts at the cathode and biofilm thickness increase, which limits proton conductivity, oxygen reduction reaction (ORR), and nutrients diffusion. Another important phenomenon, which may causes MFCs performances to worsen, is membrane biofouling, namely the formation onto the membrane surface of a layer consisting of bacteria and precipitated salts, acting as physical blockage to proton transfer across the separator.

In our case, the observed power behavior may be related to several reasons. First of all, it is well known from the literature that in case of Nafion™ and Nafion™-like PEMs, where the -SO₃H group is the main actor for the proton transport, the membrane resistance to proton conductivity could be negatively affected by the coordination of the H-binding sites to bigger cations present in the substrate, at the expense of protons [9]. Here, the best performances offered by the membrane Nafion™/SBA-SO₃H10, seem to be strictly dependent on the microstructural properties of the SBA-based filler. As already stated above,

in fact, we recently gave evidence that in SBA-SO₃H10 filler the sulphonic units are placed inside the silica mesopores [17]. Contrary to the acidic moieties of NafionTM, the silica sulphonic groups are somehow protected and consequently less available to be coordinated by the metal ions of the substrate. The actual proton transport in case of SBA-SO₃H10 composite is then improved with respect to NafionTM and NafionTM-SBA, because protons have additional pathways for the migration (given by SO₃H groups inside the pores), alternative to those otherwise blocked by bigger cations. The observed positive result is a smaller power drop under long-term operation.

The NafionTM/SBA-SO₃H50 PEM shows, in contrast, an intermediate behaviour. In this case, the filler structure is partially mesoporous and partially disordered, therefore some acidic units occupy the silica pores, whereas others are distributed along the surface, which is available for the cation coordination. The resulting performances are less stable than those of NafionTM/SBA-SO₃H10 but better than NafionTM and NafionTM-SBA (see Table 1 and Figure 3).

Another relevant factor responsible for the different electrochemical performances of the studied MFCs is biofouling. This phenomenon will be better described in the following section.

3.3 Electrochemical properties of the single-chamber MFCs: membrane morphology and effect of the membrane biofouling

As stated before, membrane biofouling deteriorates the electrochemical MFCs performances on long-term operations. The negative effect of PEM fouling was demonstrated in the literature by comparing fresh, fouled and cleaned cells. Net improvements of power output and functional stability after periodical physical and chemical cleaning steps were reported [7, 9, 23, 24].

Biofouling in our cells was studied by SEM, and remarkable different behaviors were observed depending on the type of the composite membrane. Figure 5 reports the SEM images of the membranes NafionTM (a), NafionTM/SBA-15 (b), NafionTM/SBA-SO₃H10 (c) and NafionTM/SBA-SO₃H50 (d), after 90 days of MFC operation. The electron microscopy reveals relevant biofouling in case of NafionTM and NafionTM/SBA-15, which consists of microorganisms with different morphology.

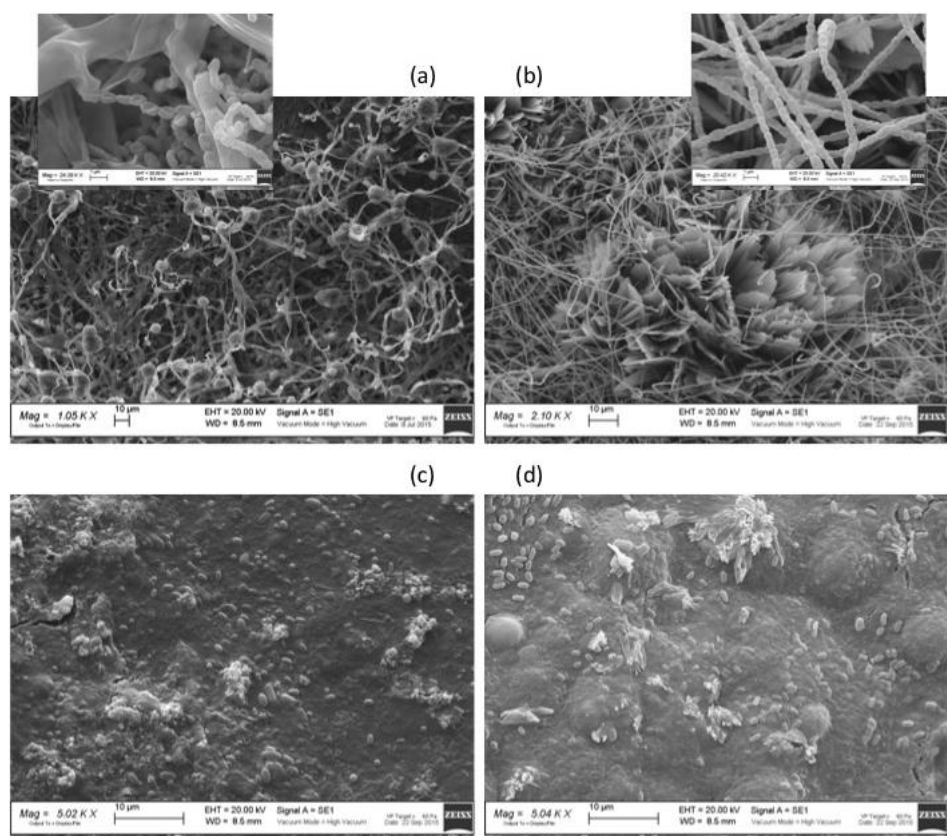


Fig.5: SEM images of membrane surface exposed to the substrate after the long-term experiments. a) Nafion™; b) Nafion™/SBA-15; c) Nafion™/SBA-SO₃H10; (d) Nafion™/SBA-SO₃H50.

From a preliminary analysis, we may observe that in case of Nafion™ (Figure 5a), two types of aerobic populations seem to coexist, round-shaped (~10 μm) and spore-like ones, growing onto a layer of fair sized rod-shaped cocci (~1 μm), which stick on the membrane surface and form long chains (inset of Figure 5a). Similar situation is observed for Nafion™/SBA-15 (Figure 5b), whose surface is also covered by a dense network of chains of rod-shaped bacteria (inset of Figure 5b), twisted around salts crystals precipitated from the organic substrate. In contrast, the separators Nafion™/SBA-SO₃H10 (Figure 5c) and Nafion™/SBA-SO₃H50 (Figure 5d) are populated by few, isolated and unstick rod-shaped cocci of 1-2 μm.

The biofouling extent of the membranes is in agreement with the power results obtained by the polarization process. In fact, the membranes revealing the highest losses of performances (93% and 83% for Nafion™ and Nafion™/SBA-15, respectively) are also those with the greatest biofouling. The reduced biofouling in membranes with functionalized filler justifies the better MFC results, in particular for the sample Nafion™/SBA-SO₃H10.

The different PEMs resistance towards biofouling can be explained in terms of different mechanisms of the microorganism adhesion, depending on the physico-chemical

properties of the membrane surface. Each Nafion-based membranes are similarly hydrophilic, as proved by comparable contact angles of about 85° , reported in table 1. This result seems to suggest that the separator hydrophilicity is not the main cause governing the bacteria adhesion onto the membrane. On the other hand, the sulphonated silica fillers show negative Z-potential (-16.2 mV for SBA-SO₃H10 and -19.9 mV for SBA-SO₃H50), contrary to SBA-15 whose Z-potential is +3.5 mV [17]. We can speculate that it is the tendency of such materials to be negatively charged, when the surface is exposed to water, to prevent the adhesion of the microorganisms (negatively charged) on the membrane, due to electrostatic repulsions. This phenomenon could consequently lead to a remarkably reduced bacteria population with respect to the unfilled membrane and also to NafionTM/SBA-15. It is known from the literature that one of the possible strategies to prevent the initial biofouling is, in fact, the anti-adhesion approach, by modifying the electric properties of the PEM surface [8].

3.4 MFC efficiency: COD removal and coulombic efficiency

Measurements of chemical oxygen demand (COD) were carried out in order to check how the herein investigated MFCs are efficient in the treatment of the urban wastewater. Figure 6 reports the COD removal during the first two operation weeks, defined as the ratio between the removed and influent COD, that determines the amount of fuel converted into bioelectricity by MFC. This parameter is necessary to calculate the coulombic efficiency, ε , that expresses the actual electrochemical efficiency of the purification treatment.

The COD measurements confirm that the best performances are offered by the membrane NafionTM/SBA-SO₃H10, whereas the worse ones by the unfilled NafionTM. After 14 days of operation, they show COD removal ability higher than 90% and lower than 80%, respectively. The differences in the removal efficiency are more evident during the first working days, as shown by the inset of the Figure 6 that points out removal percentages higher than 30% only for the membranes filled by sulphonated SBA. A similar trend is also obtained in terms of COD removal rate, $COD_{r.r.}$, whose values are reported in Table 1 for all the investigated systems.

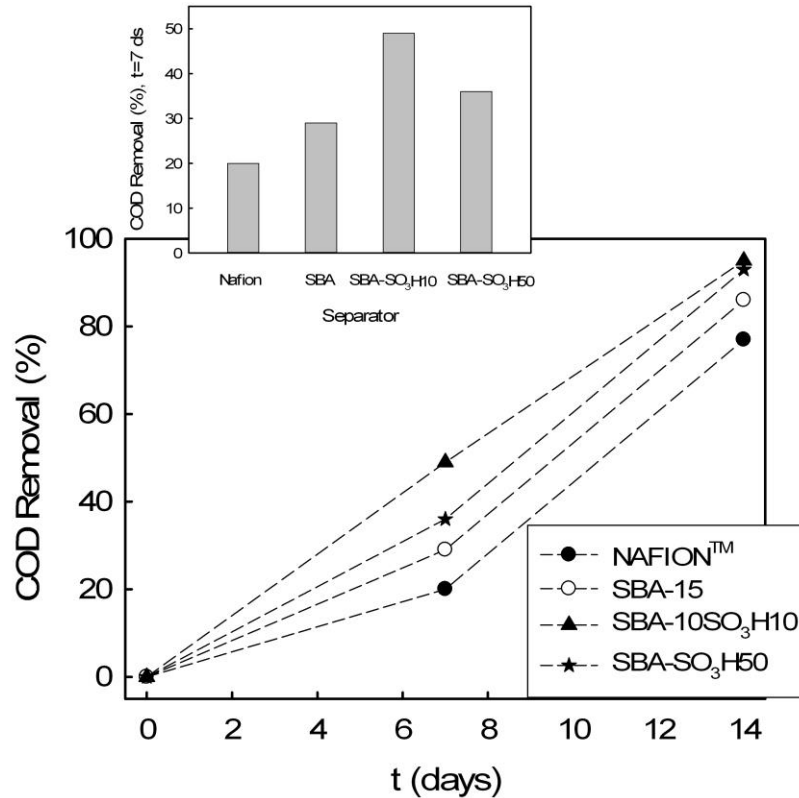


Fig.6: COD removal efficiency for the investigated MFCs with time. Unfilled Nafion™ (filled circles); Nafion™/SBA-15 (open circles); Nafion™/SBA-SO₃H10 (triangles); Nafion™/SBA-SO₃H50 (stars). The inset shows the removal efficiency measured after 7 days vs. the type of PEMs used in the cell.

As known, the COD is used to determine the MFC coulombic efficiency, ε_c , defined as the ratio of the total charge actually transferred to the anode from the substrate, to the maximum possible charge obtained if all the substrate removal produces current [4].

Table 1 reports the coulombic efficiency of the studied MFCs, calculated as described in the experimental section. ε_c ranging between 22% in case of unfilled Nafion™, and 34% for Nafion™/SBASO₃H10 were obtained over 14 days of operation. The value obtained for the MFC with Nafion™/SBASO₃H10 is very promising. Indeed, the MFCs coulombic efficiency reported in literature for wastewaters as substrate typically is less or equal 20% during the first 2-3 weeks of working time [4, 25]. The high efficiency we observed is further demonstration of the positive effect of our sulphonated filler (SBA-SO₃H10) on the performances of the corresponding composite membrane as separator for MFC.

3.5 MFCs Internal resistance

Electrochemical impedance spectroscopy (EIS) was used to estimate the internal resistance, R_i , of the investigated MFCs, which is a useful to determine the contributions of

each cell components in presence of non-linearity of the polarization plots. Several Nyquist plots were collected each week, all over the whole operation period. The spectra obtained once the cell acclimation was achieved, and at the end of the long-term experiment are reported in Figures 7 and 8, respectively. As known from literature [26], in case of air-cathode based MFCs, R_i is representative of at least four contributions, namely the activation and the diffusion resistances related to the polarization at both bio-anode ($R_{a,a}$, $R_{a,d}$) and bio-cathode ($R_{c,a}$, $R_{c,d}$), the ohmic resistance (R_Ω) and the middle components resistances, e.g. the ion-exchange membrane (R_m), as described by the following equation 2 [26]:

$$R_i = R_\Omega + R_m + R_{a,a} + R_{a,d} + R_{c,a} + R_{c,d} \quad \text{eq.2}$$

The Nyquist plots obtained on the whole MFC after the acclimation (Figure 7) only show the intercept on the Z real axis at high frequency, whose values are listed in Table 1. This could suggest that the high ohmic and membrane resistances would be predominant on the interfacial processes at the cathode and anode. Such a phenomenon was frequently observed in the literature in case of R_Ω of about $10 \Omega \text{ cm}^2$ and, in some cases, it was treated by using the R_Ω -corrected Bode plots, even if the interpretation could lead to errors in the determination of the resistive contribution [26]. At the end of the long-term experiment (about 90 days), similar values of R_Ω and R_m are obtained.

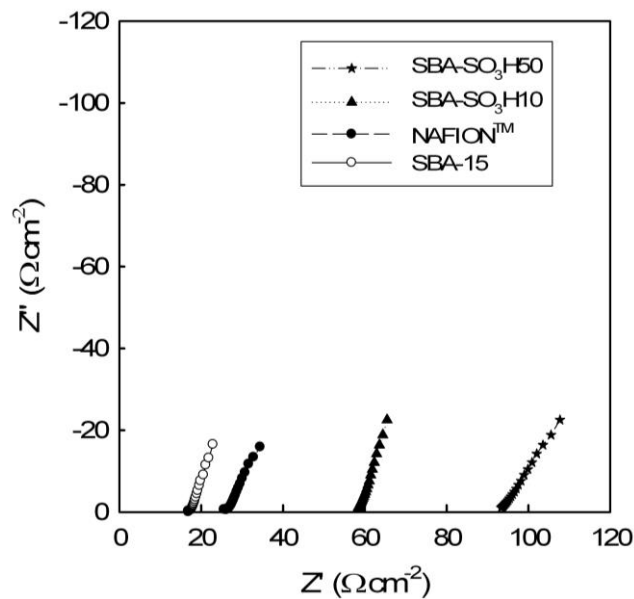


Fig.7: Impedance spectra of MFCs based on different PEMs after that cell acclimation was achieved. Unfilled Nafion™ (filled circles); Nafion™/SBA-15 (open circles); Nafion™/SBA-SO₃H10 (triangles); Nafion™/SBA-SO₃H50 (stars). The impedances are normalized with respect to the cathode surface. **Corresponding frequency of the last Z value collected in each plot: 10 mHz.**

In contrast, the semicircles related to the electrodes contribution become well evident, because the corresponding resistances increase up to values comparable to R_Q and R_m (Figure 8).

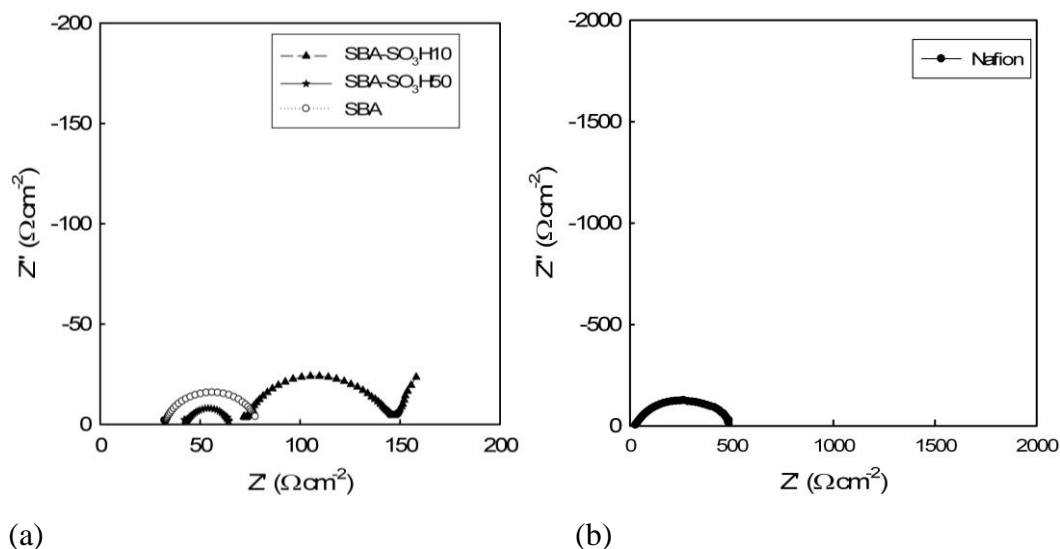


Fig.8: Impedance spectra of MFCs based on different PEMs after 90 days of operation. (a) Nafion™/SBA-15 (open circles); Nafion™/SBA-SO₃H10 (triangles); Nafion™/SBA-SO₃H50 (stars). (b) Unfilled Nafion™ (filled circles). The impedances are normalized with respect to the cathode surface. Corresponding frequency of the last Z value collected in each plot: 10 mHz.

Higher impedance may be observed in case of cell including Nafion™, with respect to the composites membranes. In particular, a resistance value exceeding 450 Ω cm⁻², related to the electrode polymerization, was measured for the unfilled Nafion™-based cell. Such differences may be somehow interpreted also in terms of thicker biofouling layers on Nafion™ compared to the Nafion™/SBA-based fillers systems, as shown by SEM images.

4. Conclusions

Four Nafion™-based PEMs, the unfilled system and different composites, were tested as separators for air-cathode microbial fuel cells, operating in fed-batch mode for urban wastewater treatment. The composites were prepared by dispersing into Nafion™ 5 wt% of mesoporous silica (SBA-15) and of the same silica functionalized with two different molar contents of sulphonic groups (10 mol% SBA-SO₃H10 and 50 mol% SBA-SO₃H50). The long-term functional performances of the composite-based cells were investigated in terms of OCV, power output, treatment efficiency, internal resistance and biofouling, and compared to

those observed for unfilled NafionTM, in order to address the actual role of the filler on the separator properties.

MFCs including NafionTM composites with sulphonated silica produced higher power than the pure NafionTM and the SBA15-based one. In particular, the NafionTM/SBA15-SO₃H10 membrane showed the best performances. Here, the filler does provide the following benefits:

- i) the membrane delivered a maximum power density of about 1 W m⁻³ with a power drop of ~60% after 90 days, against the much bigger performance worsening (93%) observed in case of the unfilled NafionTM;
- ii) NafionTM/SBA15-SO₃H10 also offered the best treatment efficiency with the highest COD removal (more than 50% after 7 days and more than 95% after two weeks) and the highest coulombic efficiency, namely 34%, which is an excellent result in case of natural wastewater;
- iii) Finally, the use of sulphonated silica preserves the membrane surface from biofouling, contrary to what occurs for NafionTM and NafionTM-SBA-15, whose surface is covered by a dense microbial colony and inorganic salts precipitated from the substrate, which affect the cell performances over long-term operation.

In the light of these experiments, we may conclude that the use of the mesoporous SBA-SO₃H fillers is a successful approach to produce composite PEMs separators for more stable and more performing MFCs to use in the wastewaters treatment. Such results further invite to explore this family of sulphonated additives also in other polymers, cheaper than NafionTM, in order to make this kind of technology more sustainable.

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