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Assessment of innovative graphene oxide composite membranes for the improvement of direct methanol fuel cells performance

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ABSTRACT

The main objective of the study was to verify potential of GO-PEM and its best effective usage in a Direct Methanol Fuel Cells (DMFC) application so investigating the effect of this filler on cell performance, varying several operating conditions, without affecting the mechanical and electric properties of the baseline PEM. In this work, GO was added to the Nafion polymer using a weight percentage varying from 0.5 to 1.5%. The present analysis showed that the GO-membranes have higher tensile strength, greater water, and methanol uptake. It was also demonstrated that the presence of carbon compounds slightly reduced the proton conductivity suggesting that an optimal GO-content must be determined. Comparing several physical and electrochemical properties, we concluded that the 1 wt. %GO-loading PEM represents the most effective solution. Later, the advantages of adopting GO-PEMs in DMFCs were also assessed. A comparative analysis of a GO-DMFC and a standard DMFC was carried out by changing the relevant control parameters, such as anode flow rate, temperature, and methanol concentration obtaining that: a) the GO-DMFC performance enhanced when increasing the temperature and the anode flow rate; b) an increase in methanol concentration had a beneficial effect on DMFC performance only up to a peak value after that a rapid reduction was noticed. Optimal conditions were obtained for an anode flow rate of 7 μl min^{-1}, a temperature of 60 °C and a 1 M methanol concentration.

1. Introduction

1.1. Background

In recent years, Direct methanol fuel cell (DMFC) technology attracted a lot of interest [1] due to its favorable characteristics, such as low operating temperature and good efficiency. In fact, a DMFC is an electrochemical system that produces energy by oxidizing a liquid fuel (i.e., a mixture of water and methanol) without the need of a pre-reforming. The use of DMFC has several advantages if compared with Hydrogen FC: easy fuel storage and management, lower cost of methanol, operation at low temperature and pressure, small system size and low weight [2]. Furthermore, methanol is considered as a very convenient and sustainable alternative fuel as it can be produced by using green hydrogen, CO, and CO_2 through the implementation of CCU (carbon capture and utilization) strategies [3]. DMFC can be advantageously used for mobile and portable applications due to the mix of good efficiency as well as weight, and volume energy densities [2]. However, several issues hinder the development and the spreading of this technology. The most relevant of such issues is related to the characteristics of the Membrane Electrode Assembly (MEA) that is based on the adoption of Nafion, a perfluorosulfonic polymer [4], as electrolyte. Nafion performs a selective transport of hydrogen ions (H^+ – i.e., a proton) from the anode to the cathode while hindering electrons conduction. Moreover, Nafion has high chemical resistance and good water permeability. However, this material is permeable to the passage of methanol (cross-over) so, during the FC operation part of the fuel crosses the membrane and reaches the cathode. There, the methanol reacts with the oxygen without producing electricity, while releasing heat, and strongly reducing the DMFC performance. Another issue in the use of methanol in FCs is related to the high catalyzer concentration required to obtain an efficient anode fuel reforming (if compared with Hydrogen) and this circumstance results in increased costs due to the request of critical raw materials (i.e., Pt and Ru) and relatively high temperature to favor the fuel reforming at the anode. These limitations, especially methanol crossover, represent a strong obstacle to the commercialization of DMFC technology and further research and innovation efforts are required [5].

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1.2. A short review on polymeric membrane for PEM fuel cells

A literature review revealed that the current research activities are focused on developing innovative composite polymer electrolyte membrane (PEM) materials able to limit the methanol crossover and to operate at low temperature [6]. Most of the related research activities were focused on the addition of inorganic or organic filler to Nafion, possibly also increasing the proton conductivity. Studies on organic fillers considered the inclusion of PTFE [7,8], polyvinyl alcohol (PVA) [9,10], and PBI [11]. These materials were used to supply reinforcement and allow higher stability of the Nafion matrix. In recent years, two types of sulphonate fillers, sulphonate poly arylene ether ketone (SPAEK), and sulphonate poly ether ether ketone (SPEEK), have been developed and used to modify the Nafion membrane structure in DMFCs. Both SPAEK and SPEEK show good properties: high proton conductivity and methanol resistance for SPAEK [12,13]; good mechanical properties, high proton conductivity, and good processing capacity for SPEEK polymers [14,15]. As for the inorganic fillers, metal oxides, such as SiO_2, TiO_2, WO_3 [16], are used to improve the capability of the membrane to retain water due to their hydrophilicity. Some authors [17,18] claimed that zeolite membranes can be adopted for DMFC application to take advantage of the molecular sieving property of zeolite in preventing methanol cross-over.

1.3. Composite graphene oxide membranes for DMFC applications

A very interesting alternative for the improvement of the Nafion performance in DMFC consists in the development of graphene oxide (GO) casted membranes. GO is a graphene derivative [19] having oxygen functional groups that can improve the water retention of a membrane, due to its hydrophilicity, even though the proton conductivity is generally reduced. Kumar et al. [20] investigated the variation of water uptake (WU), ionic exchange capacity (IEC) and cell performance by employing membranes with a GO loading ranging between 2 and 6% (2, 4 and 6% wt.). By varying the GO loading, the measured water uptake values were 21.1, 27.9, 37.2 and 36.1% respectively, while the measured ion exchange capacity (IEC) values were 0.891, 1.21, 1.38 and 1.26 meq g^{-1}. The authors argued that after reaching the optimal filler content, any addition results in increased membrane stiffness and reduced water uptake. Fuel cell tests at 100 °C and 25% relative humidity (RH) showed that the power density of a 4% GO composite membrane (212 mW cm^{-2}) is nearly 4 times higher than the reference Nafion DMFC (56 mW cm^{-2}). Moreover, several authors [21,22] reported that the use of GO can also contribute to enhance the impermeability of Nafion PEMs to the passage of liquid fuels, so reducing the methanol crossover, but at the expense of proton conductivity because of its increase in ohmic resistance due to the presence of various oxygen groups (hydroxides, epoxides, carboxyls and carbonyls). Choi et al. [21] analyzed the performance of membranes at 70 °C with a GO loading ranging between 0.1 and 2% and evaluated the effect of that filler on methanol permeability and power output. Their study also revealed that at 25 °C the methanol permeability of Nafion 112 membrane was reduced to 60.2% after the addiction of 0.5 wt% of GO. However, the proton conductivity tests revealed an opposite trend. When increasing the GO filler content up to 2% wt., a decrease of 55.3% in proton conductivity was measured. Lin et al. [23] prepared a dual-layer laminate membrane using GO, disposed in a parallel ordered configuration, as a methanol barrier for a DMFC operating at high methanol concentration. Authors demonstrated the methanol permeability of the GO membranes is reduced and 70% lower than that of the Nafion 115 while the selectivity was 40% higher. Therefore, GO can effectively block methanol passage through the membrane. This result led to an enhancement of the energy performance when operating at high methanol concentration, so when the crossover phenomenon is predominant. Several researchers used a modified GO or added this filler as a further modification to a composite Nafion membrane. Sahu et al. [24] carried out similar tests by using membranes with a GO loading between 0.5 and 1.5 wt% of GO (functionalized by sulfonic acid-containing aryl radicals). Moreover, GO particles were also blended with membranes to improve stability and ionic conductivity. Gokulakrishnan et al. [25] developed SPEEK membranes incorporating functionalized GO particles investigating thermal stability, proton conductivity, ion exchange capacity, methanol permeability to characterize the material. However, they did not analyze the mechanical properties of the composite material and the advantages it brings. Cell voltage and power density tests were carried out to evaluate the influence of GO on the energetic performance comparing the results with those obtained from a pristine SPEEK membrane. Prapainainar et al. [26] fabricated GO-mordenite composite membranes. The authors claimed that the presence of the filler benefited the proton migration through the membrane whilst for low GO content (0.01–0.25%), the methanol permeability decreased due to the well dispersion of the filler into the matrix allowing to block the flow of methanol through the membrane. Poly(diallyldimethylammonium chloride) (PDDA) and graphene oxide (GO) were added to the Nafion membrane by Yuan et al. [27]. The bilayers membranes were able to produce a methanol crossover current density of 73.0 mA cm^{-2}, which was three times lower than that recorded with the pristine membrane demonstrating a decrease in methanol crossover of about 63% confirming an efficient blocking of the methanol crossover In addition, it was demonstrated that the temperature [28], the methanol concentration [29], and the mass flow rate [30] affect the proton conductivity and the methanol crossover and, ultimately, the DMFC performance.

1.4. Aim of the work

The literature review previously discussed highlighted the potential of graphene oxide as a filler for PEMs. However, there is still a lack of information regarding the assessment of the optimal operating conditions (obtained by separately analyzing the influence of the previously cited parameters) for maximizing the performance of a GO-DMFCs.

The aim of this work is then to develop GO-Nafion composite membranes (with different GO-loading) to be used in DMFC and to assess their properties (in this work, a complete overview of all physical, mechanical and electrochemical properties was performed) as well as the optimal operating conditions. For a better interpretation of the results, a comparison with two baseline Nafion membranes (casted and commercial - Nafion 117) was carried out. The membranes were produced, chemically and physically characterized, and tested in-situ by using a single cell DMFC.

2. Materials and methods

2.1. Materials

Membranes were produced by mixing GO (commercial sheets purchased from Sigma Aldrich) with Nafion dispersion (purchased from Fuelcell Store) (D1021 10% in water). MEAs were produced assembling using GDE (Gas diffusion electrode) consisting of a GDL (Carbon cloth) and catalysts purchased from Fuelcell Store. Catalysts concentration of Pt-Ru (4 mg cm^{-2}) and PtC (4 mg cm^{-2}) were adopted at the anode and the cathode respectively.

2.2. Preparation of the membranes

The membranes were produced by solution casting. This method [31] consists in a preliminary solvent evaporation, and a successive formation of a membrane through the procedure described in the following. A Nafion ionomer dispersion was mixed with ethanol and left in a vacuum desiccator over night to remove any dissolved gas. The GO was weighted to achieve the desired loading in the composite membrane and then it was dispersed in DI water (4 mL) using an ultrasonic probe according to the protocol summarized in Table 1.

Table 1
Sonication protocol.

GO solution sonication treatment		
Time	Amplitude	Pulser
5 min	40%	5 on, 5 off
4 min	40%	5 on, 1 off
GO + Nafion solution sonication treatment		
Time	Amplitude	Pulser
2 min	20%	5 on, 1 off

In this study, three different GO fractions in the membrane were considered: 0.5, 1.0 and 1.5 wt%. For all the membranes (GO-based and Nafion bare), the following curing procedure is adopted: 2 h at 100 °C and 1 h at 120 °C. Afterwards, the membranes were treated at 80 °C by immersion in liquids in the sequence here reported (each procedure lasted 1 h): water, 3 wt% hydrogen peroxide, water, 0.5 M sulphuric acid solution, and water. After a washing, the produced membranes were immersed in water overnight.

2.3. *Membranes characterization*

The main properties, such as water and methanol uptake, ion exchange capacity, proton conductivity, microscopic structure, and tensile strength, were evaluated to properly assess the membrane quality. WU and MU (methanol uptake), proton conductivity and IEC allow to characterize a proton exchange membrane due to the influence of water on the proton transport. Analysis of the microscopic structure and measurement the tensile strength were carried out to understand the dispersion of GO in the Nafion matrix and the improvement of mechanical properties which has a direct influence on the membrane durability.

2.3.1. *Scanning electron microscope (SEM)*

A scanning electron microscope (SEM) was used to record surface morphology information of the materials [32]. The aliquots were obtained by cutting samples with ceramic knife and placed on the stubs for SEM analysis. SEM was successfully used to investigate particle distribution throughout the thickness of the membranes at both nanometre and micrometre scale. The analysis was carried out through an Electron microscopy analyzer using a Zeiss EM10 SEM, in the following operating conditions: 20 kV acceleration voltage, beam current between 6 and 14 pA and BSD detector with four elements, gain +3. By analyzing the cross sections of the composite membranes by SEM, the distribution of the filler particles was evaluated.

2.3.2. *Thermogravimetric analysis (TGA)*

The thermal stability of the membranes was tested by using a Mettler TGA/DSC1 Star in the following conditions: 50 cc min^{-1} of air flow and heating up to a maximum of 800 °C at a ramp of 10 °C min^{-1}. Membrane samples of about 10 mg were used for each test.

2.3.3. *Water and methanol uptake*

WU and MU were gravimetrically determined by recording the wet and dry mass of the membranes using the following procedure (in triplicate): the membranes were placed in water (for WU) and in a 1 M methanol (for MU) solutions at room temperature for 24 h and after that their wet weight was measured. To measure the wet weight, the water on the surface was absorbed by using dry filter paper. After this, the wet membrane samples were dried at 100 °C (until no more weight variation was detected) and their dry weight was recorded. The uptake (WU and MU) was then calculated using Eq. (1), where W_{wet} and W_{dry} denote the wet weight and the dry weight, respectively.

$$\text{Uptake\%} = \left(W_{\text{wet}} - W_{\text{dry}}\right)/W_{\text{dry}} \tag{1}$$

2.3.4. *Ion exchange capacity*

Membranes IEC was evaluated by acid-base titration method. The desired membrane was soaked in a 0.1 M HCl solution for 24 h. After the membrane was rinsed with water and then immersed in saturated NaCl for 72 h to exchange the H^+ ions for Na^+ ions. Then, the proton release was evaluated by titrating the solution with a 0.01 M NaOH solution at room temperature with phenolphthalein as indicator. The IEC was obtained by using the Eq. (2):

$$\text{IEC} = \left(V_{\text{NaOH}} - M_{\text{NaOH}}\right)/W_{\text{dry}} \tag{2}$$

Where, V_{NaOH} is the volume of NaOH titrated, M_{NaOH} is the molar mass of NaOH and W_{dry} is the sample dry weight.

2.3.5. *Tensile strength*

The mechanical properties of membranes are important parameters for polymeric films Generally, those properties are characterized by considering tensile strength and elongation capability indicating the maximum stress to which a material can resist and the maximum strain that the polymer sample can achieve before breaking [33,34]. These tests were performed by using a Zwick/Roel Z010 following the standard method D882-02. 5 samples of membranes with different GO loading were cut in strips of uniform width, 11 mm, placed in the grips of the machine and tested at a strain rate of 1 mm min^{-1}.

2.4. *Fuel cell set-up*

The MEAs were produced by hot pressing the membrane in the mid of the anode and cathode (commercial electrodes from FuelCell Store). The fuel cell electrochemical performance (cell voltage and electrical current) was measured using an in house-built station shown in Fig. 1. The test bench was controlled through the software LabView. The mixing tank contains the methanol–water solution properly prepared according to the concentration desired. From here a pump, able to process low flow rates (4 mL min^{-1} to 180 mL min^{-1}), leads the methanol solution into a heat exchanger fed by a thermostatic bath. Here the fluid temperature is increased up to the desired value (not higher than 70 °C to avoid methanol evaporation). Eventually, the fuel arrives to the cell anode and the outgoing discharging products are sent to the mixing tank, thus closing the circuit. A set of sensors is used to monitor cycle operating parameters, such as chemical concentration (through methanol sensor), temperatures (T) and the inlet pressure (P). The cell is assembled in passive mode to exploit the effect of air natural convection. The TTi LD300 Electronic DC Load is used to determine the polarization curve in the fuel cell mode. The power density was calculated as the product of cell voltage and current density. The power density was plotted against the current density (P–I curve) to determine the peak power density (Pmax) in all the test conditions.

2.4.1. *Single cell tests*

The single cell tests were carried by using the test bench described before. The adopted bipolar plates (Fig. 2) were composed of graphite with single serpentine (same pattern for both anode and cathode side) flow channels to guarantee a proper reactants distribution.

The MEAs had an active area of 9 cm^2 and their performance was tested in the fuel cell single cell sample holder. The I-V curve was recorded in triplicate for each sample. To study the effect of the operating condition on the performance of the composite membrane, tests were carried out by varying the anode flow rate, temperature, and methanol concentration. All the results were compared with that obtained from the Nafion casted membrane.

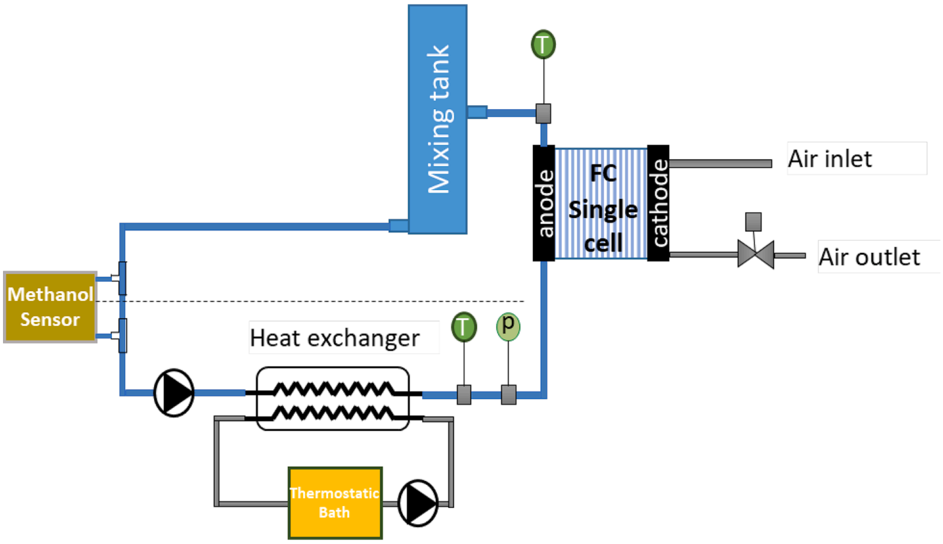

Fig. 1. Test station.

Fig. 2. Bipolar plates.

3. Results and discussions

3.1. *Membrane characterization*

3.1.1. *SEM analysis*

In Fig. 3, the images of the SEM analysis carried out for the GO-Nafion composite membranes with different GO loading (0.5, 1 and 1.5 wt%) are shown.

The filler particles were evenly distributed into the Nafion matrix (the blank one), through the thickness of the membrane. The GO-particles were orientated horizontally thus creating “layers” enhancing the cross-over suppression. This effect is more emphasized for the membrane with 1 wt% of GO. However, large agglomeration regions are present especially at 1.5 wt% of GO loading.

To further analyse this trend, a SEM from a different angle of Fig. 3B is carried out (Fig. 4). The plot clearly shows how the GO particles are distributed in parallel layers, following the structure of the membrane.

3.1.2. *Thermogravimetric analysis (TGA)*

The comparison among the TGA plots obtained by the treatment of the composite membranes here analyzed showed similar trends for GO loading of 0.5%, 1% and 1.5%. Some differences are noticed in two different temperature ranges. Firstly, in the range between 50 and 150 °C there was a decrease in mass due to water evaporation, that is slightly higher for the membrane with a 0.5% GO-loading. This is since in this loading configuration it is easier to remove the water molecules trapped between the GO layers. When the temperature increases up to 300 °C a strong decrease in mass was observed due to the incremental loss of functional groups (in all the membranes) before the complete destruction of the polymer chain. This phenomenon is more pronounced for the 0.5% GO-loading case. At temperature higher than 500 °C, there was still some residues of the composite membranes especially 1.0% and 1.5% GO-loading, while again the 0.5% GO-loading almost disappeared in analogy with the case of bare Nafion membranes, where no residue is noticed above 500 °C [10]. This circumstance confirms the guess that a noticeable GO content improves the thermal stability of the membrane (See Fig. 5).

The thermal stability of 1.5% GO loading case is slightly lower than 1. 0% GO loading case. Despite this behaviour is not in agreement with the expectations, the difference is very low. It can be attributed to dis-uniformities in the fabrication process or to the loss of GO surface functional groups.

3.1.3. *Water and methanol uptake*

The membrane characteristics in terms of water and methanol uptake are shown in Table 2.

Preliminary, we notice that the casted Nafion membrane shows a WU value that is much lower than the commercial one due to a not perfect manufacturing process at lab scale. Then, in the successive considerations, only the casted membranes produced in the same lab, are considered for comparisons. From the analysis of the results in Table 2, it is possible to see that the addition of GO led to a clear increase of the water uptake when compared with the nafion casted. Small addition of GO loading, 0.5 wt%, led to an increase of WU of around 5%. At 1.5 wt% of GO, the WU increase is equal to 23%. This is due to the hydrophilic nature of GO as confirmed in the work of Peng et al. [35]. According to

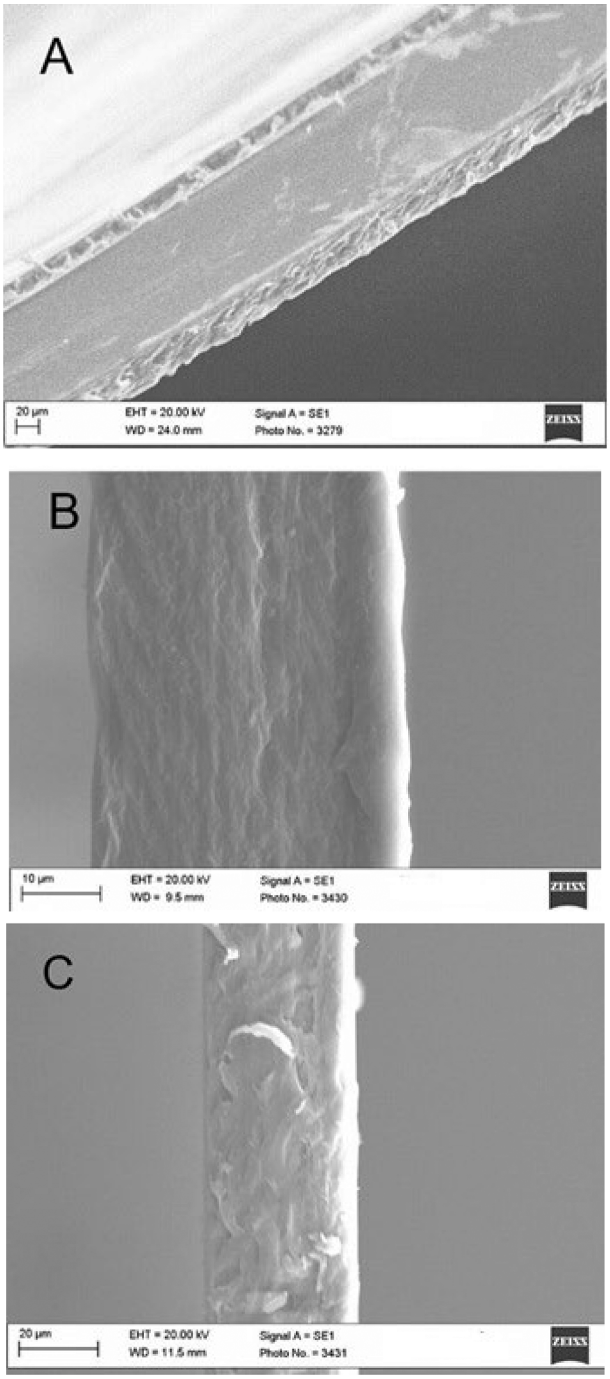

Fig. 3. SEM images for recast and GO membranes. A for 0.5%, B for 1% and C for 1.5%.

the literature, an increase in the GO content, up to 4%; can lead to an increase in the WU. However, above that value, the behavior is reversed because of the amphiphilic nature of the Nafion membrane [36]. The results shown in Table 2 show that generally, the water uptake of the membranes (Nafion and GO-casted) is higher than the methanol uptake, indicating that the membranes preferentially adsorbed water molecules. However, the GO addition contributed to increase the methanol uptake, especially in the cases of 0.5 wt% and 1.0 wt%, where MU shows a value that is almost double that recorded for the Nafion casted membrane. Such result is relevant as MU (along with methanol permeability) is a factor that indicates the ability of methanol solution to diffuse through the membrane. As methanol is soluble in water, therefore, it can be dissolved and move along with water. The higher is the methanol absorbed by the membrane, the lower is the methanol crossover from anode to cathode side. Interestingly, the MU showed a peak at 0.5 and 1.0 wt% but, when further increasing the GO-loading a relevant reduction is noticed. This trend may be due to a non-perfect shrinkage of the ionic channels among all the samples analyzed. The results obtained are in agreement with the work of Gokulakrishnan et al.[25] in which a decrease in methanol permeability was recorded when increased the content of functionalized GO from 0 to 2 wt% due to the existence of the silane group leading a better interaction of GO with the polymer. Since the enhancement was very slow, the WU and the MU were evaluated also for membranes with 3 and 4% of GO loading to better comprehend this trend. The trend observed was with the previous tests was confirmed: the WU increased when increasing the GO content while the MU led to an opposite trend.

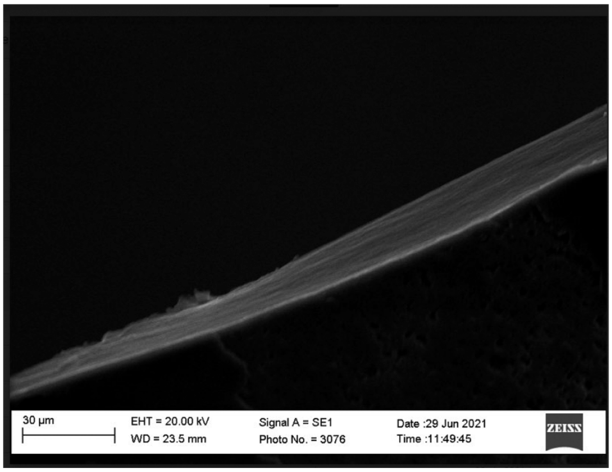

Fig. 4. Different outlook of Fig. 3B.

3.1.4. *IEc*

In Table 3 the IEC values of the analyzed membranes are shown.

The IEC increases with the increase of the GO content. The highest value, 1.07, was obtained with a GO content of 1.5 wt%, reaching an enhancement of 30% if compared with the bare casted Nafion. Also in this case, membranes with 3 and 4% of GO loading were tested to deepen the effect of the filler on this property. The behavior was confirmed by increasing the GO loading value up to 4 wt%. leading to a maximum of 1.29.

The beneficial effect of GO on the IEC is controversial. In contrast with the present results, Ibrahim et al. [37] noticed that the IEC decreased with the addition of GO when compared to the recast Nafion. They attributed this behavior to two possible reasons:

i. the lower Nafion content in the GO composite membranes
ii. the reduction in ionic channels consequent to the incorporation of GO in the Nafion.

Their analysis was, however, inconclusive. On the other hand, in agreement with the present work, Kumar et al. [24] showed that the addition of GO contributes to improve the IEC.

There are several possible causes to explain the incongruity among this work and the above-mentioned literature works:

i. A non-uniformity in the graphene oxide dispersion within the composite membrane: in fact, for this type of test, just a small piece of membrane was used (2 samples, 1x1 cm). A non-uniform dispersion with agglomerates could potentially have a higher IEC as less ionic channels are obstructed by the graphene oxide.

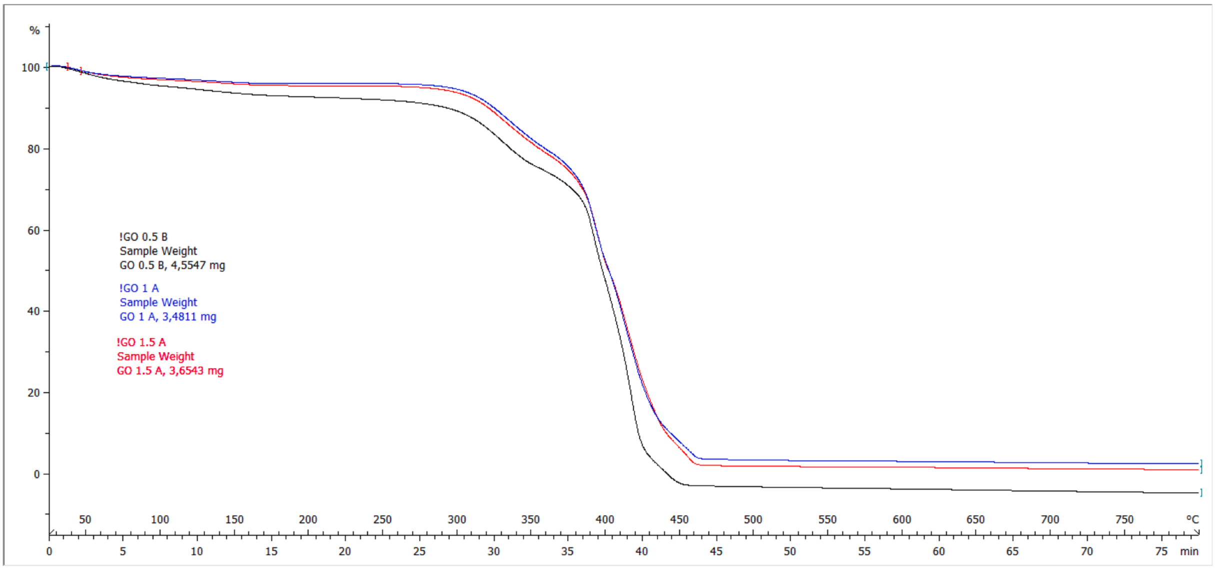

Fig. 5. TGA images for recast and GO membranes. Black for 0.5%, Blue for 1% and Red for 1.5%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Water uptake of Nafion 117, casted Nafion and casted GO membranes.

Membrane	Water uptake/%	Methanol uptake/%
Nafion 117	38	–
Nafion casted	24.1 ± 2.07	5.1 ± 1.7
GO membrane 0.5 wt%	25.4 ± 1.85	10.1 ± 1.52
GO membrane 1 wt%	27.4 ± 2.08	9.9 ± 1.37
GO membrane 1.5 wt%	29.6 ± 1.67	6.7 ± 1.85
GO membrane 3 wt%	30.5 ± 1.94	5.3 ± 0.56
GO membrane 4 wt%	32.3 ± 0.83	4.9 ± 0.89

Table 3
Ion exchange capacity of Nafion 117, casted Nafion and casted GO membranes.

Membrane	IEC/meq g^{-1}
Nafion casted	0.83 ± 0.12
GO membrane 0.5 wt%	0.92 ± 0.07
GO membrane 1 wt%	0.99 ± 0.08
GO membrane 1.5 wt%	1.07 ± 0.18
GO membrane 3 wt%	1.18 ± 0.22
GO membrane 4 wt%	1.29 ± 0.14

ii. The Nafion solution is 10% in water, but that might not be the amount of Nafion samples (e.g. it could be 9% or 11%). This is due to the density difference between Nafion and water. This consideration can be applicable also for the WU.

iii. As the titration stopped when the solution turned to a bright pink, some errors due to the human eye may be occurred.

3.1.5. Proton conductivity

The DMFC performance is strongly dependent on the proton conductivity. In fact, high proton conductivity means high voltage per current density. A literature review was carried out to understand the effect of the GO filler on that property. Choi et al. [21] measured the proton conductivity at 25 °C and claimed that in composite membranes such property slightly decreases when the GO content increases eventually reaching a decrease of 55.3% with 2 wt% of GO loading. A similar trend is also remarked by Hattenberg et al. [38] that observed the influence of the organic filler on proton conductivity, at both low (80 °C) and intermediate temperatures (120 °C). All the composites showed lower proton conductivity than the Nafion sample. Table 4 lists the results obtained for the proton conductivity from the works above mentioned.

In a Ph.D. work carried out at University of Birmingham under the supervision of one of the authors on the same class of membranes, Hattenberg, [38] observed that the proton conductivity generally increased with the temperature up to a certain value (80 °C for a Nafion bare membrane) but especially decreased as the GO content increased (18% of reduction for a membrane with 0.5 wt% of loading while a 36% of reduction was observed for a loading of 5 wt%). Comparing the results obtained by the works cited, it is highlighted that the content of the filler mitigates the drop on proton conductivity when increasing the temperature making GO composite membrane attractive for high temperature operations. However, direct methanol fuel cells, used in this work, are a type of PEM working at low temperature. Therefore, regarding the proton conductivity, the results obtained from Choi et al. [19] are more helpful for the aim of this work. But, since the tests of the authors were carried out at lower temperature than that implemented in this work, the trend observed by Hattenberg was also considered for the discussion about the optimum filler loading.

3.1.6. Tensile strength

In all the GO-Nafion membrane a tensile strength higher than the bare Nafion membrane is expected due to the inclusion of GO into the perfluorosulfonic matrix. Then, the higher is the GO included in the membrane, the higher tensile strength is expected. The tensile strength and the elongation ratio of the recast Nafion and composite membranes

Table 4
Proton conductivity of casted Nafion and casted GO membranes.

Membrane	Proton conductivity/S cm^{-1} Hattenberg [33]	Proton conductivity/S cm^{-1} Choi [19]
Nafion casted	0.040	0.042
GO membrane 0.5 wt%	0.034	0.040
GO membrane 1 wt%	Missing	0.033
GO membrane 1.5 wt%	Missing	0.026
GO membrane 2 wt%	Missing	0.023
GO membrane 3 wt%	0.032	Missing
GO membrane 5 wt%	0.030	Missing

were summarized in Table 5.

The obtained results agree with the previous findings and with the results present in the work of Wang et al., [39] where the same trend was observed: the tensile strength was 12.5 MPa for the Nafion membrane and 16, 17.5 and 19 MPa for the GO membranes with a loading of 2.3, 3 and 5% respectively.

On the contrary, it is observed that the elasticity of the GO membrane is very low compared to Nafion. Again it is in agreement with literature. Bayer et al. [40], observed that the elongation of the pure GO membrane before rupture is only 22 ± 1%, compared with 41 ± 14% measured in Nafion membrane.

3.1.7. Influence of graphene oxide on the properties of a membrane

For the following discussion, the membrane with 3% and 4% wt. of GO were excluded due to the fact that the proton conductivity is too low to be considered for fuel cell application. The overall analysis carried out on the impact of GO loading on the membrane performance allows to claim that the increase of GO-loading leads to: a) WU, MU and IEC increase; b) proton conductivity decrease. Fig. 6 reports the trend of WU, MU and proton conductivity at different GO loading here considered.

In Table 6, a comprehensive analysis of the percentage deviation (with respect to casted Nafion membrane) of WU, MU, proton conductivity, IEC, tensile strength, and elongation of all composite membranes, is shown.

From the analysis of the previous results, it is possible to conclude that the choice of 0.5 and 1 wt% GO loading represents a good compromise between gains and losses. Similar findings were obtained also by Choi et al. [19], that analyzed several configurations with GO-loading varying in the range 0.1–2% and obtaining that the best physical and transport properties were obtained by a Nafion/GO composite membrane with 0.5 wt% of GO loading. Such membrane showed the highest selectivity (the ratio between proton conductivity and methanol permeability) but the difference with the one with 1% GO-Loading was only 10%. Even though the membrane with 1% had lower methanol permeability, also the proton conductivity is reduced limiting the positive effects of increasing GO-loading. Lee et al. [41], analyzed the performance obtained from a direct methanol fuel cell, using Nafion/GO membranes at 0.5, 3 and 4.5 wt%. Their results agree with the present findings and showed that the reduction in methanol crossover enhanced the performance of the composite membrane, but at 4.5% the drop in proton conductivity was too high despite a low methanol permeability. In their case, the optimum GO-Loading was equal to 3%.

From the literature review and the present results we can conclude that to improve the DMFC performance it is essential reducing the fuel crossover, also accepting a reduction in the proton conductivity. The morphological analysis showed that the GO is better dispersed in the membrane with 1% rather than that at 0.5%, contributing to block the methanol crossover. Therefore, after considering all the results listed in Table 6 and pondering the great impact of methanol crossover on the performance of the cell, we decided to fabricate our GO-DMFC by using 1 wt GO-loading membranes.

3.2. Assessment of the GO-DMFC performance

The theoretical open circuit voltage (OCV) of a DMFC (1.21 V), computed by using the Nerst equation, is almost similar to the value calculated for an H_2 PEMFC (1.23 V). However, several drawbacks such as the methanol crossover, the engulfment of the fuel passage due to the generation of CO_2 at the anode are the most relevant causes of performance reduction. As told, here we focus on the assessment of effect of methanol crossover.

Table 5
Tensile strength and elongation ratio of the fabricated membranes.

Membrane	Tensile strength/MPa	Elongation ratio/%
Nafion	13.77 ± 3.03	75 ± 6.9
Nafion- GO 0.5 wt%	15.90 ± 0.66	65 ± 8.7
Nafion- GO 1 wt%	17.53 ± 3.06	50 ± 10.9
Nafion- GO 1.5 wt%	18.37 ± 2.74	40 ± 4.3

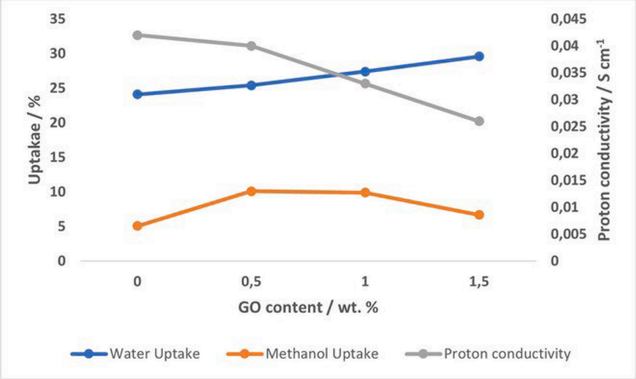

Fig. 6. Proton conductivity, water uptake and methanol uptake of Nafion/GO membranes at different GO loading.

To this end, we decided to investigate the effects of varying the anode flow rate and the methanol concentration, that are parameters directly influencing the OCV condition and the power output, and then they represent an indirect indication of the crossover. The operating range were set according to the previous experience of the authors on DMFCs.

3.2.1. Anode flow rate

To test the influence of the anode flow rate, we run the test by imposing a temperature of 40 °C and a 1 M methanol concentration.

Three different anode flow rates (AFRs) were analyzed: 4 mL min^{-1}, 7 mL min^{-1}and 15 mL min^{-1}. The minimum AFR (4 mL min^{-1}) correspond to the minimum flow rate allowed by the available pump. Fig. 7 show the power density and polarization curves associated to the cell tests for casted Nafion (Fig. 7A) and GO composite membrane with 1% of GO loading (Fig. 7B).

Fig. 7 shows that the addition of GO led to higher performance (compared to Nafion membrane) in terms of voltage and power density. Furthermore, GO-loading membrane can operate in a wider range of current density reaching about 39 A m^{-2}, while the bare Nafion did not operate at current densities greater than 33.3 A m^{-2}. The DMFC power density varies with increasing anode flow rate. The examined configurations consist of methanol flow rates of 4, 7 and 10 and ml min^{-1}. The peak performance is reached a methanol flow rate of 7 mL min^{-1} where the power densities of Nafion-casted and GO-composite are 3.5 and 4 W m^{-2} respectively. A rapid decrease in the DMFC performance is noticed when the methanol flow rate further increases to 15 mL min^{-1}. It is believed that this is since at high flow rate the methanol crossover strongly increases, even though this condition enhances the mass transport of methanol and the removal of CO_2 from the anodic channels. In addition, the methanol solution at high flow rate cools down the temperature of catalyst surface, and hence decrease the activity of the Pt-Ru catalyst.

3.2.2. Methanol concentration

The methanol molarity expresses the number of methanol moles present in the solution, representing a measure of the quantity of fuel available for a mixture flow. Here, the methanol concentration is varied while the operating conditions are fixed as follows: a) Anode Flow Rate equal to 7 mL min-1, b) Temperature equal to 40 °C.

Three different levels of concentration have been analyzed: 0.5 M, 1 M and 1.5 M. Fig. 8 shows the power density and polarization curves associated to the cell for the present analysis.

The variation of molarity leads to evident deviation in terms of both power and current density curves as well as their operating range. A high

Table 6
Deviation of proton conductivity, IEC, WU and MU of Nafion/GO membranes at different GO loading from the Nafion casted.

GO content	Water uptake	Methanol uptake	IEC	Proton conductivity at 25 °C	Tensile strength	Elongation rate
0.5 wt%	+5%	+98%	+9.8%	−5%	+48%	−13%
1 wt%	+14%	+94%	+16%	−20%	+55%	−33%
1.5 wt%	+23%	+31%	+22%	−35%	+63%	−47%

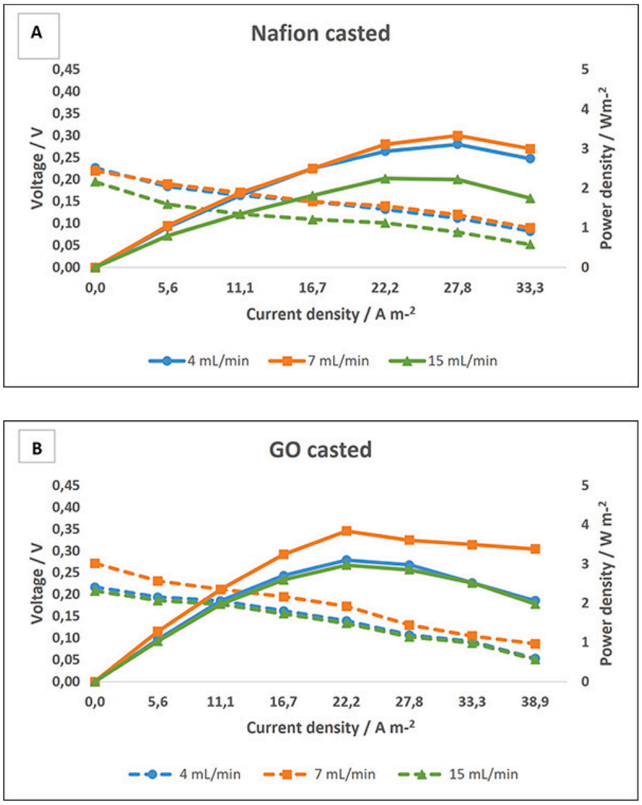

Fig. 7. Effect of anode flow rate on Nafion casted (A) and on GO-Nafion membranes (B).

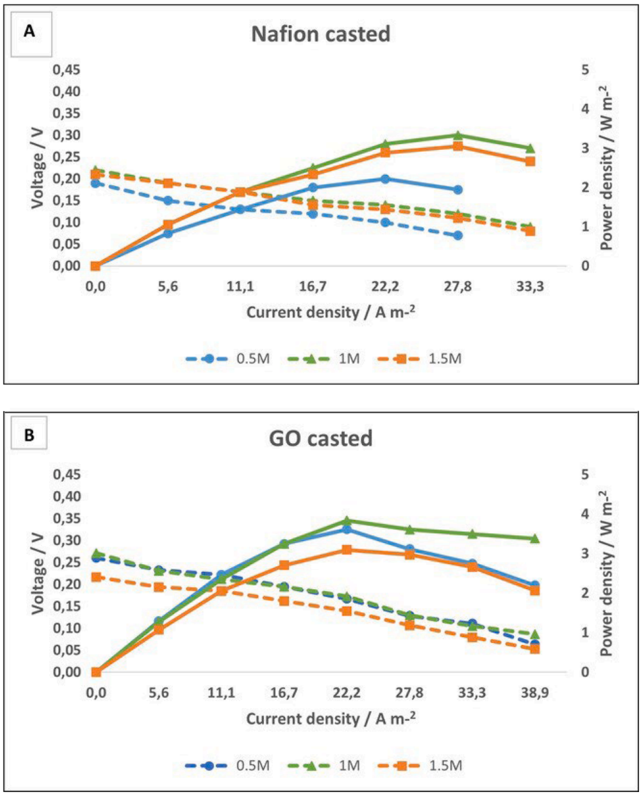

Fig. 8. Effect of methanol concentration on Nafion casted (A) and GO membranes (B).

methanol concentration enhances the reaction rate in the anode, but at the same time increases the methanol crossover towards the cathode. The methanol eventually reaching the cathode is oxidized over Pt catalyst to produce mixed potential, generating parasite currents, and decreasing the DMFC performance. In fact, when the concentration of the solution is 1.5 M, the open circuit voltage (OCV) drops for both the Go-loaded and bare Nafion membranes indicating a strong effect of methanol crossover. On the contrary, when the methanol concentration is 0.5 M, the OCV is quite low because of the scarcity of reactants. Closing the external circuit and increasing the current density, the cells' voltage varies following the polarization curve. Here, again the maximum current density is greater for GO-membrane, extending up to 38.9 A m^{-2} (while Nafion reaches a maximum of 33.3 A m^{-2} only). At the intermediate methanol concentration (1 M), the GO-DMFC performance reaches its peaks in terms of power density (3.85 W m^{-2}) and maximum current density due to the optimal balancing of the reactants availability and crossover reduction. Seo et al. [42] and Braz et al. [43] also observed the effect of methanol concentration on DMFC performance. In both works it is claimed that the reaction that occurs at the anode is limited to high methanol concentration, reaching a peak in power production for concentration 2 M and 5 M, respectively. This variance is related to the different operating conditions and the different components of the stack.

3.2.3. *Temperature*

The influence of temperature was analyzed by fixing the other analyzed parameters as follows: a) Anode Flow Rate: 7 mL min^{-1}; Chemical Concentration: 1 M.

Three different temperatures were tested: 20 °C, 40 °C and 60 °C. In Fig. 9 the power density and polarization curves associated to the FC are shown.

As told, the temperature acts as a promoter of the cell performance because of a) the increase of the catalytic activities for methanol electro-oxidation and oxygen reduction, b) the increase of ion conductivity of Nafion membrane and Nafion ionomer leading to the reduction of ohmic polarization losses in the catalyst layer.

Consequently, the DMFC performance increases significantly with an increase in cell temperature. However, the temperature was not increased over 60 °C to avoid methanol evaporation, (64.7 °C).

The enhanced DMFC performance at increasing cell temperatures can be attributed to the following two processes:

I. The increase of the catalytic activities for methanol electro-oxidation and oxygen reduction with increasing cell temperature.
II. The ion conductivity of Nafion membrane or Nafion ionomer in the catalyst layers decreases with an increase in cell temperature, so the ohm polarization loss decreases.

At low temperature, the methanol electro-oxidation rate is slow, and

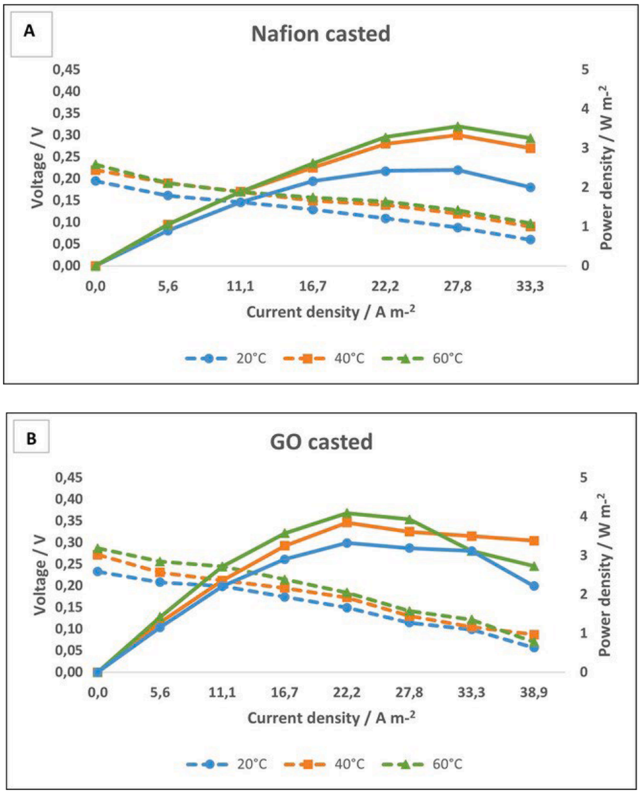

Fig. 9. Effect of temperature on Nafion casted membrane (A) and GO membranes (B).

the CO_2 in the anode as well as the water in the cathode cannot be rapidly removed. This blocks the diffusion of methanol and oxygen to the catalyst surface. When the cell temperature increases, the reactant diffusion and the product removal increase, so the electrochemical reaction is faster. All these processes contribute to the enhanced DMFC performance at high cell temperature. This result agrees with those obtained by Jung et al. [44] with Nafion 112 membrane and 1 M methanol solution in the range of 50–80 °C. Authors attributed this trend to the combined effects of a reduction of ohmic polarization and activation polarization.

3.2.4. Discussion

The above analysis investigated the effect of operating conditions on DMFC performance. Extending the anode flow rate and methanol concentration has a dual effect: increasing the flow of the reactant allows to obtain higher performance despite enhancing the methanol crossover and losses. At one point, the loss will be no longer counterbalanced, and performance starts decreasing. The appropriate operating conditions of the target DMFC are 1 M methanol at the flow rate of 7 mL/min. The greatest DMFC performance increase is attributable to an increase in cell temperature, which can be ascribed to the enhancement of the catalytic activities as well as the ion conductivity in the MEA. The optimum is obtained at 60 °C.

In addition, the use of GO-based composite membranes leads to a relevant improvement of DMFC performance in controlled operating conditions. Table 7 summarizes the relevant parameters related to the use of both GO composite membrane and the casted Nafion membrane. The results in the table are referred to the tests recorded at 60 °C where the power output of both membranes are the maximum.

Maximum power output, OCV and operating range of bare Nafion is always lower than GO membrane. This behavior is always present, but it is more evident at low methanol concentration and low anode flow rate. Notably, the impact of GO is remarkable at 0.5 M where the maximum increment is obtained: 27% for the OCV, 32% for the best power output and 16% for the operating range. It is then clear that the improvement of the performance is due to the introduction of GO in the polymeric matrix. GO contributed to enhance the retention of water and methanol and to reduce the fuel cell crossover, even though it leads to a reduction of proton conductivity. Even though the methanol crossover current density was not directly measured, the beneficial effect of the GO on the crossover is proved by the values of the open circuit voltage. In every test, the OCV of the composite membrane is higher and this is principally due to the structure of GO (showed in the SEM analysis) included into the Nafion that hinder the passage of methanol to the cathode side. In addition, it is evident the correlation between OCV, methanol crossover and power output: the higher is the increment in OCV, the higher is the power output.

Table 7
Comparison between GO membrane and Nafion casted.

Operating condition (at 60 °C)	OCV	Power output	Operating range
4 mL min^{-1}	+10%	+11%	+17%
7 mL min^{-1}	+23%	+15.3%	+17%
15 mL min^{-1}	+10%	+32.5%	+17%
0.5 M	+36.8%	+63%	+40%
1 M	+24%	+15.6%	+17%
1.5 M	+5%	+4%	+17%

4. Conclusions

The main objective of this paper was to verify the effectiveness of graphene oxide as filler material for polymeric membranes in DMFC application. The fabrication of composite GO-membranes, with a variable GO loading in a range 0.5–1.5% in weight, contributed to an extensive analysis of their mechanical, the physical, electrochemical properties and energetic. The SEM analysis confirmed the inclusion of the carbon filler into the polymeric matrix. Tests in TGA indicated that the chemical bonds in GO-Nafion samples are more stable and persistent than in the bare Nafion. The analysis of all the properties led to the conclusion that the optimum GO loading is 1%. Result achieved as a compromise between the beneficial effect of GO on water and methanol uptake and the drop of proton conductivity. The performance in the cell were evaluated to investigate the effect of the operating conditions. The increase of DMFC performance with the temperature is ascribed to the enhancement of the catalytic activities as well as the ion conductivity in the MEA. An appropriate methanol flow rate concentration is needed to reduce methanol crossover despite facilitating the mass transport. The best operating condition were 1 M and 7 mL min^{-1}. In comparison with bare Nafion, GO shows higher OCV and power output. It is believed that this is due to increased tortuosity of the GO-membrane and the consequent reduction in fuel crossover. Therefore, the drop in proton conductivity is counterbalanced by the drop in methanol crossover, that is highlighted by the OCV enhancement. This result was underlined by the SEM analysis that depicted the blocking structure of graphene oxide.

List of symbols	
C	Carbon
D.I.	Deionized
DMFC	Direct methanol fuel cell
GDE	Gas diffusion electrode
GDL	Gas diffusion layer
GO	Graphene oxide
I	Current density/A m^{-2}
MEA	Membrane Electrode Assembly
P	Power/W m^{-2}
V	Voltage/V

CRediT authorship contribution statement

G.G. Gagliardi: Conceptualization, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **A. El-Kharouf:** Conceptualization, Methodology, Supervision. **D. Borello:** Conceptualization, Supervision, Data curation, Writing – review & editing.

Declaration of Competing Interest

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.

Data availability

Data will be made available on request.

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