



Full Length Article

# An efficient composite membrane to improve the performance of PEM reversible fuel cells

Gabriele G. Gagliardi<sup>a,\*</sup>, Orlando Palone<sup>b</sup>, Enrico Paris<sup>c</sup>, Domenico Borello<sup>a</sup>

<sup>a</sup> Department of Mechanical and Aerospace Engineering, University of Rome La Sapienza, Rome, Italy

<sup>b</sup> Department of Astronautical, Electrical and Energy Engineering, University of Rome La Sapienza, Italy

<sup>c</sup> CREA, Italy



## ARTICLE INFO

### Keywords:

Composite membranes  
Durability  
Electrochemical tests  
Graphene oxide  
Polarization curves  
Unitized reversible fuel cell

## ABSTRACT

In this study innovative composite Nafion/GO membranes are tested at different GO loading (0.5% wt., 1% wt. and 1.5% wt.) in electrolyser and fuel cell mode (Unitized reversible fuel cell). Baseline Nafion membranes were used for comparison.

Water uptake (WU), ion exchange capacity (IEC), tensile strength, TGA (thermogravimetric analysis) and SEM (scanning electron microscope) analysis are discussed. The SEM revealed the inclusion of GO into the Nafion matrix while the TGA showed an increased thermal stability of the membrane attributed to the inclusion of the carbon material. Moreover, the addition of GO improves the membrane tensile strength, obtaining a maximum enhancement of nearly 90%, while reducing the elongation ratio (80% for the Nafion and 45% for the 1.5% wt. GO membrane). Water uptake increased when increasing the content of GO due to its hydrophilic nature recording the highest values for the membrane with 1.5%wt. of GO (23% against 10% for the Nafion). An increase of IEC (almost 14%) is noticed when GO content is increased. The beneficial effect of GO on the IEC can be attributed to a non-uniform distribution of GO into the Nafion matrix but needs further investigation.

Both fuel cell and electrolyser polarization curves were carried out using MEAs with an active area of 9 cm<sup>2</sup> and a thickness of 50 μm. The temperature and the pressure were set to 20 °C and 1 atm respectively. Regarding fuel cell mode, the optimum loading of GO has been found to be 0.5%, registering the highest performance, 13% higher than Nafion. Regarding the electrolyser mode, the GO 0.5% wt. membrane, showed performance comparable to the Nafion. A comparison between Nafion based membranes at higher thicknesses showed that, adopting GO, it is possible to obtain similar performance with a reduced membrane thickness, keeping almost equal the performance and the average round trip efficiency (26.1% for the GO and 26.6% for the Nafion). In commercial applications such characteristics allows to strongly reduce the cost of materials.

Durability and stability of the GO/Nafion membrane should be properly investigated in successive studies as such membranes are subjected to a rapid deterioration of their performance.

## 1. Introduction

The need to contain the effect of climate changes urges to increase the share of renewable energy sources (RES) mainly with reference to electricity production [1]. RES are by nature discontinuous and aleatory thus requiring efficient storage strategies for allowing a deferred use of electricity. Despite batteries are today considered as the most developed and promising solution for energy storage, they however present several disadvantages in terms of rapid auto-discharge, high material costs, large volumes and weights, long charge time [2]. On the other side, the storage of the surplus of energy in the form of H<sub>2</sub>, through electrolysers,

and the successive conversion in power through fuel cells (representing today the device with the highest conversion efficiency [3]) can allow to overcome batteries shortcomings. Among different types of fuel cells, the unitized Reversible PEM Fuel Cells (RFCs) could represent an innovative and promising technology able to accomplish two different tasks: power production (fuel cell mode) and energy storage (electrolyser mode) in a single device [4]. In addition to the versatility and the reversibility, this technology is characterized by several advantages such as low operating temperature, fast start ups, operation at high current densities, low volumetric density, low weight of the stack and suitability for discontinuous operation. Despite in past decades many efforts to develop the URFC-PEM fuel cell technology were carried out, its major

\* Corresponding author.

E-mail address: [gabriele.gagliardi@uniroma1.it](mailto:gabriele.gagliardi@uniroma1.it) (G.G. Gagliardi).

<https://doi.org/10.1016/j.fuel.2023.129993>

Received 22 May 2023; Received in revised form 22 September 2023; Accepted 30 September 2023

Available online 7 October 2023

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## Nomenclature

### List of symbols

C	Carbon
D.I.	Deionized
EL	Electrolysis
FC	Fuel cell
GDE	Gas diffusion electrode
GDL	Gas diffusion layer
GO	Graphene oxide
I	Current density, A/m <sup>-2</sup>
MEA	Membrane Electrode Assembly
P	Power, W/m <sup>-2</sup>
PEM	Polymeric electrolyte membrane
RT	Round trip
SEM	Scanning electron microscope
TGA	Thermogravimetric analysis
URFC	Unitized reversible fuel cell
V	Voltage, V
WE	Water electrolysis
WU	Water uptake

barriers including low overall performance, high costs for commercialization purpose and above all reduced durability have not been solved yet. In fact, to date the operational lifetime for real life applications does not meet the requirements for the commercial technologies (40,000 h for stationary applications and 5000 h for mobile applications) [5].

Despite the issues related to costs are far from a satisfying solution, new ideas and methodologies can be implemented to improve the overall efficiency and the durability of the RFCs. It is believed that the most promising improvement and the most appropriate field of novelty and innovation is obtained by improving the performance of the membrane electrode assembly (MEA) that is often considered to be the heart of the unitized regenerative fuel cell system. MEA consists of a polymeric membrane and two catalyst layers. The membrane is made of a sulfonated polytetrafluoroethylene polymer with high protonic conductivity, water permeability and chemical resistance. Nafion membranes are generally robust and stable. Only alkaline metal ions as sodium, decreasing the proton conductivity [6], and calcium [7], altering the charge distribution, can damage the Nafion at standard temperature and pressure conditions (STP) [8]). However, one of the key issues that affects the performance of the Nafion device in fuel cell mode is the gas crossover that lowers the power output of the system. This leads to the need of thicker membranes [9], but thickening the membrane leads a) to an increase of the electrical resistance and then to a reduction in efficiency and b) to higher costs of production [10]. To overcome these issues, research activities aiming at modifying the Nafion matrix were carried out for: (a) reducing the thickness of the membrane while keeping unchanged the performance through a reduction of the fuel permeability; (b) enhancing the durability. The addition of a GO filler into the membrane makes possible to overcome such drawbacks preserving the good properties of the baseline Nafion [11]. Although many investigations have been undertaken, up to now few membrane-based studies have been reported for URFC applications. In [12] organic materials were dispersed in the polymer membrane matrix to augment several important properties, such as proton conductivity, water uptake, and stability. Organic compounds have been shown to strengthen and allow increased stability of the polymer matrix, making it more cost-effective. This improves the mechanical and thermal stability of the polymeric membrane. Furthermore, the incorporation of organic material can act as a barrier for the fuel crossover in the membrane [13]. Graphene Oxide (GO) is a highly hydrophilic material and exhibits a reasonable level of proton conductivity [14]. Despite earlier work

already described the potential of composite GO/Nafion membrane in improving some properties of the Fuel Cells [11,15], no study appeared in the literature about the use of this filler for electrolysis.

The incorporation of GO into the Nafion electrolyte increases the mechanical strength, the water uptake and gas impermeability of the membrane so enhancing the performance in fuel cell mode giving the opportunity to ensure higher performance and long-term operation while reducing the thickness of the membrane eventually reducing the total cost [16]. So, considering these two aspects, it is interesting to investigate if the addition of the organic material can influence the overall performance of a device that operates in both electrolysis and fuel cell mode as the URFC.

This work analyzes for the first time in the open literature the behavior of GO-Nafion membranes when subject to electrolysis reactions and aims at verifying whether its use in RFC is indeed possible [11,15,16]. Furthermore, the assessment of the overall performance of a PEM-URFC assembled with polymeric membrane based on GO/Nafion is discussed, focusing on two of the drawbacks of the technology: the global efficiency of the device and the reduction of the membrane thickness (directly impacting on the cost of the materials). For this purpose, membranes are produced by varying the content of the organic filler. The influence of the filler on mechanical, electrochemical, physical properties and the optimum loading for an energetic use is assessed. A comparison with the Nafion bare membrane produced at different thicknesses is carried out. Moreover, several successive cycles of tests were carried out to evaluate the influence of the filler on the round-trip efficiency and the durability of the device.

## 2. Materials and method

### 2.1. Materials

Materials and precursor were obtained from several companies: GO sheets and hydrogen peroxide (34%) from Sigma Aldrich; sulfuric acid (98%) from Alfa Aesar; Nafion dispersion, GDL and catalysts, PtC at the anode and the cathode, from Fuel cell store. The choice of those electrodes arises from the need to improve the fuel cell operating mode when the utilization of GO is well known to be beneficial [14].

### 2.2. Preparation of membranes

Nafion and composite Nafion-GO membranes were prepared using casting method. This process consists in an evaporation of a solvent from a solution containing the polymer (Nafion in this case) plus the solvent (ethanol) [6]. The final thickness reached was  $50 \pm 2 \mu\text{m}$ . Regarding Nafion-GO membranes, three different loading were considered: 0.5 % wt., 1% wt. and 1.5% wt. For membranes preparation the following procedure was adopted:

- To prepare a single Nafion layer, a solution of Nafion/ethanol was firstly poured in a vial and put inside a dryer connected to a vacuum pump to allow air to be removed from the solution. Subsequently, the solution was poured into a flat Petri dish and then put in the oven, varying the amount of Nafion proportional to the target thickness of the final membrane. The amount of ethanol added is equal to half of Nafion quantity (4.9 mL). The Petri dish with the solution was placed for drying in an oven, undergoing the following heating cycle: 2 h at 100 °C, then 120 °C for 1 h.
- The protocol to prepare a single GO layer is the following: GO sheets were put, along with water, into a vial and subjected to a sonication process. Then, the content of that vial was mixed with a solution of Nafion/ethanol. After being under the dryer, it was poured into a flat Petri dish and then put in the oven. The amount of ethanol added is equal to half of Nafion quantity (4.2 mL).

Afterwards, the membranes were treated at 80 °C by immersion in

the following sequence (each procedure lasted 1 h): in water, in 3% H<sub>2</sub>O<sub>2</sub>, in water, in 0.5 M H<sub>2</sub>SO<sub>4</sub> and in water. Then, the membranes were immersed in water overnight.

### 2.3. Characterization

The main properties, such as water uptake (WU), ion exchange capacity (IEC), microscopic structure, thermogravimetric analysis (TGA) and tensile strength, were evaluated. WU and IEC are relevant tests to characterize a proton exchange membrane due to the influence of water on the protons transport. Microscopic structure is useful to understand the dispersion of GO in the Nafion matrix while TGA and tensile strength measurement were carried out for the improvement of mechanical properties which has a direct influence on the membrane durability. For better comprehension, all the data are compared with those measured in a re-casted Nafion.

#### 2.3.1. Scanning electron microscope

Scanning electron microscope (SEM) was used to record surface morphology information of the sample by recording secondary electrons emitted from the material due to inelastic scattering [17]. SEM can successfully be used to investigate particle distribution throughout the thickness of the membranes at both nanometer and micrometer scale. The analysis is carried out through 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 with SEM, the distribution of the filler particles could be evaluated.

#### 2.3.2. Water uptake

Water uptake (WU) was determined gravimetrically by recording the wet and dry mass of the membranes using the following steps (repeated three times): the membranes were placed in water at room temperature for 24 h, and then their wet weight was measured. To measure the wet weight, the water on the surface was absorbed using dry filter paper. After this, the wet membrane samples were dried at 100 °C and their dry weight was recorded. The water uptake (WU) was measured using Eq. (1), where WE<sub>w</sub> and WE<sub>d</sub> denote the wet weight and the dry weight, respectively.

$$WU = (WE_w - WE_d) / WE_d \quad (1)$$

#### 2.3.3. Ion exchange capacity

The ion exchange capacity (IEC), expressed as milliequivalent of ion exchange groups per gram of the membrane (meq/g), is an important parameter because the ionic transport properties depend on the amount of the ion exchange groups. The IEC and WU are usually correlated: an increase of IEC induces high water content, but the mechanical strength of the membrane drops [18]. Membranes Ion Exchange Capacity was evaluated by acid-base titration method. The desired membrane was soaked in 0.1 M HCl for 24 h. After thoroughly rinsing the membrane with water, it was immersed in saturated NaCl for 72 h to exchange the H<sup>+</sup> ions for Na<sup>+</sup> ions. Then, the proton release was evaluated by titrating the solution with 0.01 M NaOH at room temperature with phenolphthalein as indicator. The IEC was obtained by using the Eq. (2):

$$IEC = (VOL_{NaOH} \times M_{NaOH}) / WE_d \quad (2)$$

#### 2.3.4. Tensile strength

Tensile strength and elongation are both important mechanical properties regarding polymeric membrane because they indicate the maximum stress to which a material can resist before breaking. This test was performed using a Zwick/Roel Z010 following the standard method D882-02. 5 samples 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.

#### 2.3.5. Thermogravimetric analysis (TGA)

The thermal stability of the membranes was tested using a Mettler TGA/DSC1 Star in the following conditions: with 50 cc of air flow and heating to a maximum of 800 °C at a ramp of 10 °C/min. Membrane samples of about 10 mg were used for each test [14].

### 2.4. MEA tests

The MEA was obtained by hot pressing the membrane sandwiched between the commercial electrodes purchased from Fuelcellstore. The electrodes consist of carbon cloth gas diffusion layer with Platinum supported by carbon black as catalyst with 4 mg cm<sup>-2</sup> of loading. The current collectors were made of stainless-steel plates with a thickness of 0.5 mm. The plate geometry allows the control of the mass flow rate of the reactants through a series of holes (3 mm) machined on the active area of the current collectors. Hydrogen and oxygen tanks are integrated and have a maximum volume of 30 mL each. The electrochemical performance (cell voltage and electrical current) of the device were measured by using a test station consisting of an Agilent E3631A DC power supply to perform the electrolysis and the TTI LD300 Electronic DC Load to carry out the polarization curve in the fuel cell mode. MEAs had an active area of 9 cm<sup>2</sup>. The MEAs were tested in the fuel cell single cell sample holder. The I-V curve was recorded 3 times for each sample. All the results were compared with that obtained from the Nafion casted membrane. Both fuel cell and electrolysis tests were performed at 20 °C and at 1 atm.

## 3. Results and discussion

### 3.1. Membrane characterization

SEM images of the GO-Nafion composite membranes with different loading (0.5 % wt., 1 % wt. and 1.5% wt.) are shown in Fig. 1 and compared with the membrane casted with bare Nafion. GO sheets are correctly dispersed into the Nafion matrix, even if, in some areas, the GO is randomly dispersed and unoriented [14]. To highlight the presence of GO particles, some of them are enclosed within red circles.

The bare Nafion membrane, is generally smooth, as shown in the cross section of Fig. 1D. When adding the graphene oxide, the filler particles were distributed into the Nafion matrix creating parallel layers. However, the distribution of the layers is not uniform, in fact, as depicted in Fig. 1B, the particles are dispersed only in one part of the cross section (highlighted with a red circle) while the remaining part looks empty of GO. This characteristic is principally related to the homemade preparation of the membrane that needs further optimization in order to control GO orientation. It is arguable that an improvement in membrane manufacturing, e.g by controlling the orientation and the disposal of the GO layers, can further increase the properties of such component [19].

Table 1 displays the membrane characteristics of water uptake and IEC. In all cases, the presence of GO in the polymer structure has led to an enhancement of both water uptake, due to the hydrophilic nature of graphene oxide, and IEC [20].

The trends observed for both the parameters agree with those obtained in a previous work [14]. As for the IEC trend an unexpected behaviour is noticed. Since incorporation of GO dilutes the -SO<sub>3</sub>H groups of Nafion matrix, the IEC should decrease when increasing the GO content. There are some possible causes of this deviation:

- 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 (3 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.
- The Nafion solution used to prepare the membranes is 10% wt. in water, but that might not be the amount of Nafion contained into the

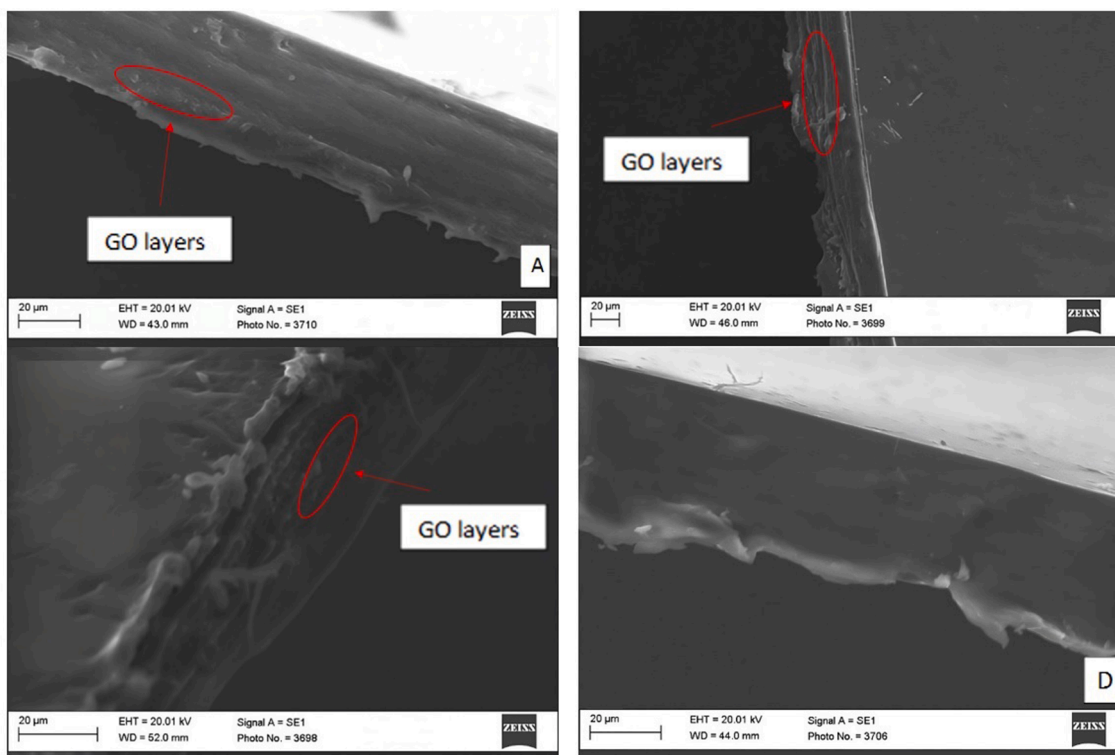


Fig. 1. SEM images for recast and GO membranes. A for 0.5% wt., B for 1% wt., C for 1.5% wt., D for bare Nafion [14].

Table 1

Water uptake and ion exchange capacity of the fabricated membranes.

Membrane	Water uptake %	IEC (meq/g)
Nafion	10	0.80
Nafion-GO (0.5%)	13	0.87
Nafion-GO (1%)	16	0.89
Nafion-GO (1.5%)	23	0.91

samples (e.g. it could be 9% or 11%). This is due to the density difference between Nafion and water.

An improved manufacturing process can help to make clear the effect of the filler on the IEC.

The tensile strength and elongation ratio data of the recast Nafion and composite membrane are shown in Fig. 2.

All GO/Nafion membrane showed a tensile strength higher than the bare Nafion membrane due to the inclusion of GO into the perfluorosulfonic matrix. The more GO is included in the membrane, the higher tensile strength is obtained, as stated by several authors, see e.g., [21,22]. However, as can be observed in Fig. 2, the elasticity of the GO membrane is very low compared to Nafion. These results agree with literature and with a previous work carried out on Nafion/GO membranes [14]. For a better understanding of the results, Table 2 summarizes the key values registered from the above tests.

TGA results are shown in Fig. 3. The y-axis represents the mass percentage of the sample, the x-axis the experimental time in minutes (as reported in Materials and methods, the TGA run using a ramp of 10 °C/

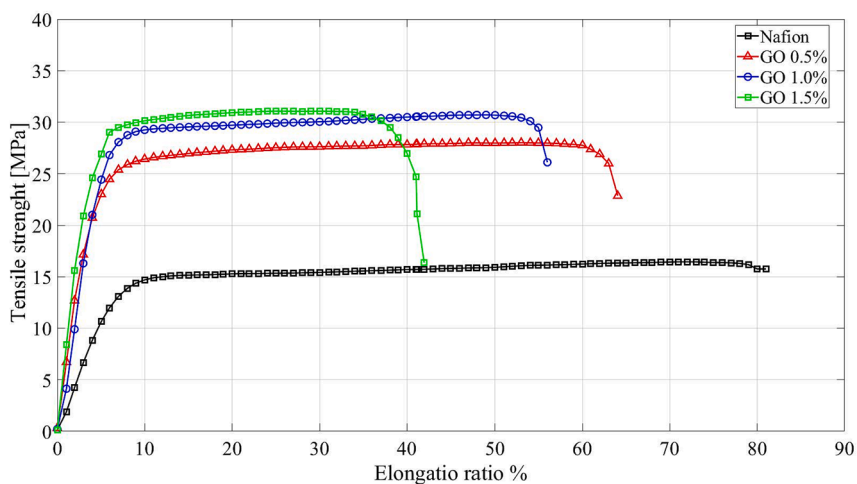


Fig. 2. Tensile strength and elongation ratio trends of the fabricated membrane: Nafion with a black line, GO 0.5% with a red line, GO 1% with a blue line, GO 1.5% with a green line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 2**

Final results of tensile strength and elongation ratio of the fabricated membranes.

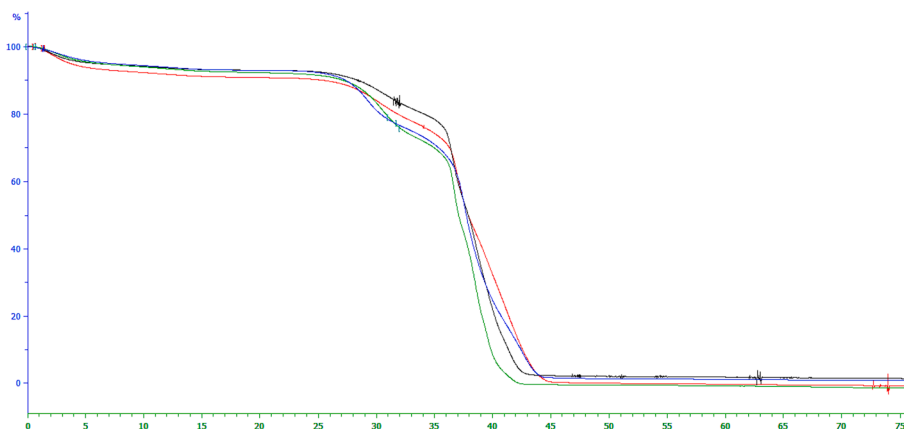
Membrane	Tensile strength [MPa]	Elongation ratio (%)
Nafion	16.55	80
Nafion-GO (0.5%)	28.10	67
Nafion-GO (1%)	31.16	53
Nafion-GO (1.5%)	31.88	45

min) The explanation of the trend registered were deeply analyzed in the work of Gagliardi et al. [14] and showed that high GO improves the thermal stability of the membrane, meaning that the mass decrease of the GO membranes is lower than that of the bare Nafion.

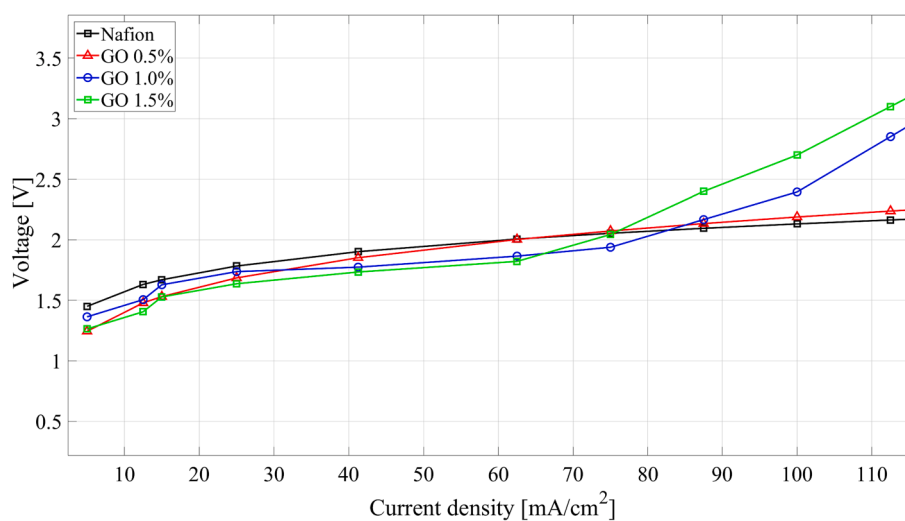
### 3.2. In-situ tests

The current–voltage (I-V) characteristics curves for the prepared GO and Nafion casted composite membrane are studied in both electrolysis and fuel cell mode. The curves shown in this section are obtained as the average of three repetitions. Single cell water electrolysis polarization curves were reported in Fig. 4.

As the GO content was increased, the voltage required for the water



**Fig. 3.** TGA tests. Nafion is depicted with the green line, GO 0.5% with a red line, GO 1% with a blue line, GO 1.5% with a black line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



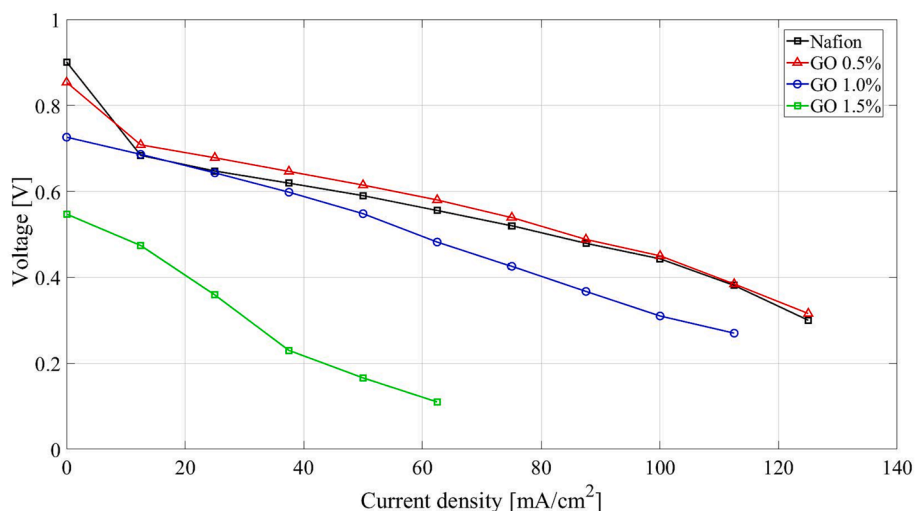
**Fig. 4.** Effects of different GO content on water electrolysis (the cell operated with purified water at 20 °C and atmospheric pressure). Nafion with a black line, GO 0.5% with a red line, GO 1% with a blue line, GO 1.5% with a green line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electrolysis also increased. In the activation region, the voltage is slightly higher for the cell with plain Nafion, even if there are no remarkable differences among all the membranes; whereas at higher current densities, higher voltages are required for the cell assembled with the GO composite membranes. The cell with 1.5% wt. of GO loading showed the highest energy request for water electrolysis. Due to the low proton conductivity of the GO, the inclusion of the filler lead to an increasing derating of the electrolysis reaction. This phenomenon needs to be better elucidated, carrying out tests at different temperatures because, the lowering of the proton conductivity of the membrane is emphasized at low temperature. However, the results from Fig. 4 underlines that the modification of the membrane with the inclusion of 0.5% wt. of GO does not significantly vary the power needed for the water electrolysis.

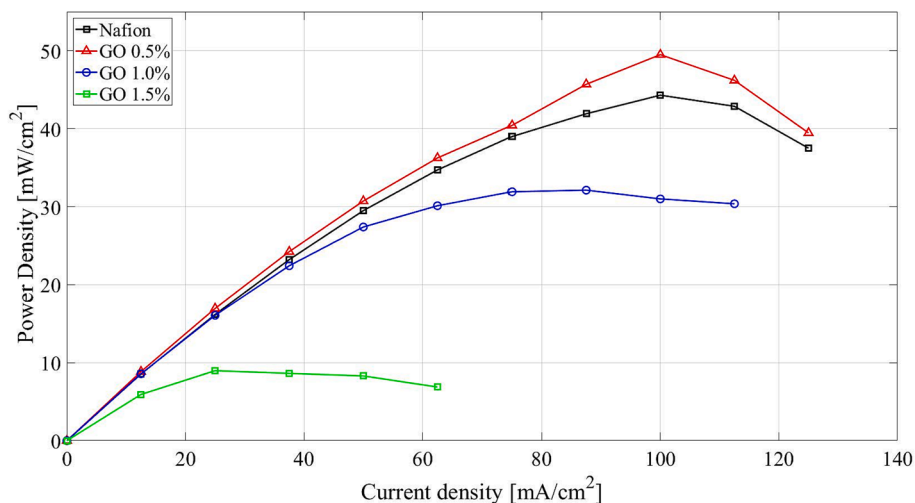
Fig. 5 and Fig. 6 show the fuel cell polarization and power curves of single cells with different GO contents and for pure Nafion membranes. The membranes have a thickness of 50  $\mu\text{m}$ .

The performance of the single cell was slightly increased with a GO content of 0.5% wt. When the current density was 100  $\text{mA}/\text{cm}^2$ , the power output recorded was 49.5  $\text{mW}/\text{cm}^2$  for the composite membrane while 43.75  $\text{mW}/\text{cm}^2$  for the bare Nafion. This was because the graphene oxide retained more water and enhanced the ion exchange capacity, so those beneficial effects mitigate the drop in the proton





**Fig. 5.** Fuel cell polarization curves for Nafion, Nafion-GO membrane with 0.5%, 1% and 1.5 wt. (the cell operated with at 20 °C and atmospheric pressure). Nafion was plotted with a black line, GO 0.5% with a red line, GO 1% with a blue line, GO 1.5% with a green line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 6.** Fuel cell power curves for Nafion, Nafion-GO membrane with 0.5%, 1% and 1.5 wt. (the cell operated with at 20 °C and atmospheric pressure). Nafion was plotted with a black line, GO 0.5% with a red line, GO 1% with a blue line, GO 1.5% with a green line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

conductivity [20]. As expected, a further increase of the GO content leads to a drastic reduction of the performance. In fact, the maximum power density, and the operating range of the composite membrane with 1% wt of GO loading, were 35% and 10% less than those recorded for the best performing membrane. Even more evident is the collapse registered for the membrane with 1.5% of GO content, where the percentage deviations of maximum power output and operating current range were minus 80% and 50% respectively, compared with the best Nafion performance obtained. This trend can be ascribed to two different reasons:

- 1) The gain obtained by the enhancement in water uptake are not able to counterbalance the loss in proton conductivity that increases when the GO content grows, as shown in a previous work [14];
- 2) The ohmic resistances of the cell are more relevant when the quantity of the filler is high. The slope of the V-I curves on Fig. 4 was evaluated because it represents the ohmic term corresponding to the total resistance of the cell. The Nafion and the GO 0.5% wt. show an identical slope of about  $3.5 \Omega \cdot \text{cm}^2$ , while the slope of the GO 1% and 1.5% were  $4.3$  and  $7.4 \Omega \cdot \text{cm}^2$ , respectively. The higher values can be

attributed to the structure of graphene oxide that influences the proton conductivity. Hattenberg et al. [23] investigated the effect of this organic filler claiming that the proton conductivity dropped when increasing the GO content. To overcome this issue, the use of sulphonating graphene oxide can increase the sulfonic acid groups, which play a key role on the transport of the protons through the ionic channel, so increasing the proton conductivity [24,25]

In general, the literature about URFCs always used Nafion membranes varying mainly their thickness to obtain different mechanical performances or long-term stability. An exception to this trend is present in the study carried out by Lee et al. [12]. They have proposed a Nafion membrane modified with polypyrrole (PPy) using Pt/C as catalyst. The fuel cell tests were performed under ambient pressure at 80 °C while electrolysis was performed at ambient pressure and 60 °C. Regarding the fuel cell mode, when the cell voltage was 0.313 V, the current density was  $636 \text{ mA/cm}^2$ , therefore a power output of  $200 \text{ mW/cm}^2$ , registering a value four times higher than that recorded in this work. However, it is well known how temperature increases performance. In our tests it was

not possible to control the temperature, so the huge difference of the energetic performance can be ascribed to that operating condition. The energetic performance registered in the electrolysis mode for the GO membrane and the polypyrrole are equal at  $100 \text{ mA/cm}^2$ . Although the trend is similar, Lee et al. were able to operate in a wider current density range. Also in this case, temperature played an important role, enhancing the kinetics of the semi reactions.

As shown in Fig. 6, the addition of GO contributes to enhance the performance of the cell. Foarooqui et al. [15], claimed that the addition of this material can also guarantee the utilization of a thinner membrane, ensuring the same performance, therefore lowering the costs. Fig. 7 and Fig. 8 compare polarisation and power curves of single cells obtained for MEAs assembled with Nafion casted membranes at different thickness (50 and  $100 \mu\text{m}$ ) and the one assembled with the optimum GO loading (0.5% wt.) and a thickness equal to  $50 \mu\text{m}$ .

Fig. 8 illustrates that the Nafion membrane with the highest thickness ( $100 \mu\text{m}$ ) showed the best performance,  $50.8 \text{ mW/cm}^2$ , compared to the membranes (Nafion and GO composite) produced with a thickness of  $50 \mu\text{m}$  ( $43.75 \text{ mW/cm}^2$  for the Nafion and  $49.5 \text{ mW/cm}^2$  for the GO composite). The result was predictable since, as well known, the thinner is the membrane, the higher is the gas crossover then the lower is the power output [26]. So, the advantage of including the filler into the Nafion matrix would be not so evident. However, the maximum performance obtained from the Nafion bare membrane with  $100 \mu\text{m}$  is  $50.8 \text{ mW/cm}^2$ , only 2.6% higher than the one recorded for the GO 0.5% wt. ( $49.5 \text{ mW/cm}^2$ ). A very small gap obtained halving the thickness of the membrane and these results can be optimised by adjusting the GO membrane thickness. Considering that result, taking into account the cost of the Nafion solution adopted (D1021,  $1.27 \text{ €/mL}$ ) and of the GO sheets ( $0.35\text{€/mg}$ ), Table 3 reports the costs of the materials needed to produce the two different membranes:

The tiny diminution registered for the power output is balanced by the money saving: the production cost of a GO-Nafion membrane is almost the half of that of the pure Nafion.

Together with performance and costs, the last relevant aspect to be analysed is the durability. Fig. 9 shows the maximum FC power density (with a membrane thickness of  $50 \mu\text{m}$  and STP) along 10 operating cycles (every cycle was performed in triplicates) to investigate the energy performance drop of the device. Every single cycle consists of the electrolysis operation, performed to produce hydrogen, followed by fuel cell polarization curve.

As shown in Fig. 9, the maximum power density delivered by the fuel cell assembled with the Nafion membrane remains stable along all the

cycles analyzed, slightly dropping after the 7th cycle. The 0.5% GO composite membranes shows the highest power density along almost all the tests. However, all the GO/Nafion configuration show a continuous drop in the performance up to the last cycle. This suggests that more effective manufacturing technologies should be carried out to reduce the degradation.

Table 4 summaries the initial and the final value registered for the power output, highlighting the percentage deviation.

The performance of Nafion does not suffer substantial decrease, and it is reduced by only the 16%. Furthermore, the power output registered after the tests is higher than that recorded for the composite membrane with 0.5% wt. of GO. The marked reduction of the performance related to the composite membranes was expected due to electrochemical carbon corrosion at high voltage, one of the critical determinants of the lifetime of polymer electrolyte membrane fuel cells [27]. This phenomenon is not attributed to the fuel cell conditions, in fact carbon usually corrodes at potentials that are close to 1 V (open circuit condition for a fuel cell) but is related to the electrolysis operations, where the potentials were higher than one so increasing the oxidation rate of carbon. This behavior is emphasized for the membrane with 1.5% wt. of GO loading, where the performance registered a collapse of more than 80%.

By considering the results obtained in both WE and FC, the round-trip efficiency (RT) was calculated as the ratio between the energy granted during fuel cell mode and the energy absorbed in the electrolysis mode. Table 5 listed the average RT calculated along all the tests carried out.

Despite the small improvement registered in the first cycle and an average value similar to the Nafion one, the RT is still far from reaching an acceptable value for URFC commercialization and global uses, especially if we consider the fact that it should be kept constant for hundreds of hours. Further investigations are required. Performing tests at higher temperatures can highlight the benefit of the addition of GO in high temperature and long-term utilization due to the enhanced thermal stability of the membrane, a crucial parameter for several applications. As for instance, the next generation of automotive, powered by PEMFC, aims at increasing the operating conditions up to  $105 \text{ °C}$  while reducing the membrane thickness to increase the MEA performance [16]. In addition, to increase the durability of the system, a possible strategy is to modify the membrane itself as mentioned above. As the main drawback of the GO is the low conductivity of the material, two possible routes are possible to overcome this problem: reduction and sulfonation of graphene. The reduced graphene oxide (rGO) is obtained by partially

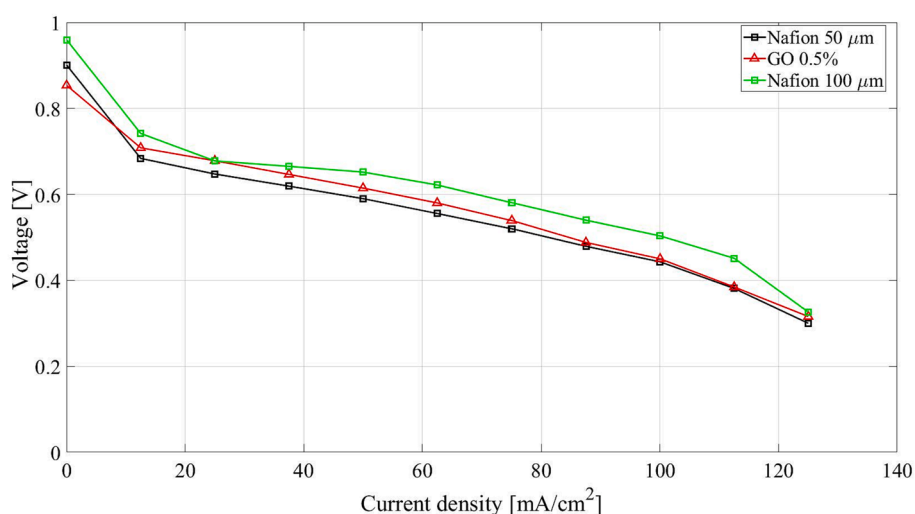
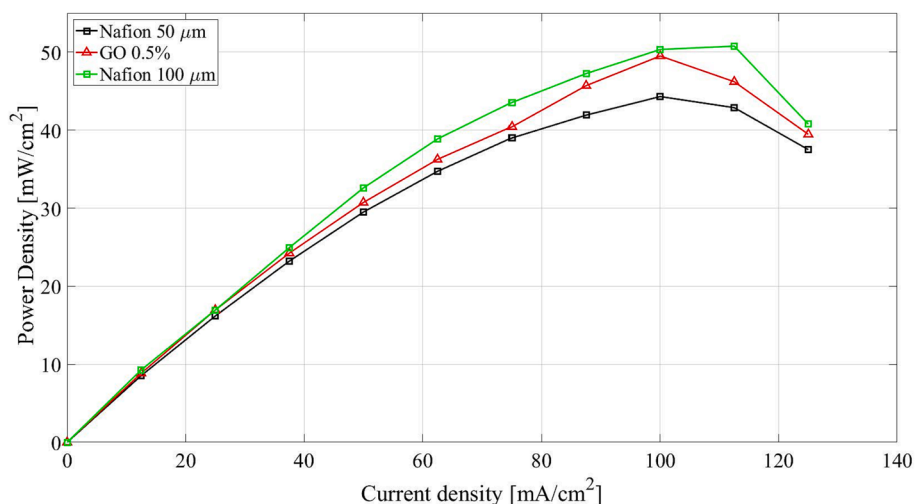


Fig. 7. Fuel cell polarization curves of different membranes (the cell operated with at  $20 \text{ °C}$  and atmospheric pressure). Nafion membrane with  $50 \mu\text{m}$  of thickness was plotted with a black line, GO 0.5% with a red line, Nafion membrane  $100 \mu\text{m}$  of thickness with a green line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 8.** Fuel cell power curves of different membranes of different membranes (the cell operated with at 20 °C and atmospheric pressure). Nafion membrane with 50 μm of thickness was plotted with a black line, GO 0.5% with a red line, Nafion membrane 100 μm of thickness with a green line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 3**

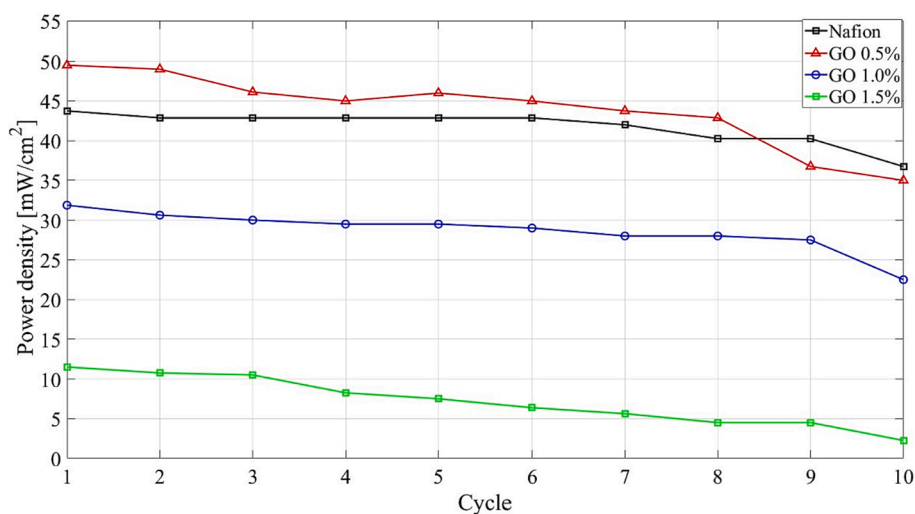
Costs of Nafion and GO-Nafion membranes.

Membrane	Amount of Na	Amount of GO	Total cost per membrane	Total unit cost
Nafion 100 μm	9.53 mL	/	12.10 €	1.34 €/cm <sup>2</sup>
GO 0.5% wt.	4.2 mL	2.59 mg	6.24 €	0.69 €/cm <sup>2</sup>

removing the oxygen-containing functional groups and recovering the needed sp<sup>2</sup> carbon atoms, thus recovering electrical conductivity properties [28]; the sulfonation methods is a process of modification of GO with sulfonated groups (SO<sub>3</sub>H) in order to improve the chemical link at the catalyst interface for the preparation of electrodes for fuel cells, so further enhancing electrical conductivity and the surface area [26]. Since the carbon corrosion is another issue that affects the performance of this technology, another approach can be to replace the carbon with titanium as GDL, proved to ensure longer lifetime of the device [27].

#### 4. Conclusion

In this study, Nafion and GO-Nafion membranes were fabricated via solution casting and tested in a PEM reversible fuel cell. The membranes were characterized, and it was confirmed that, through the SEM, graphene oxide was successfully incorporated into the Nafion structure. The composite membranes exhibited better tensile strength and higher water uptake, but with lower elongation. TGA analysis showed a better thermic resistance. In-situ testing revealed that the composite membrane with 0.5%wt. GO loading had the highest FC performance allowing to reduce the thickness of the membrane so the costs. Since WE performance is comparable to the bare Nafion membrane, a slight improvement in term of efficiency is registered, even if with a lower durability due to the carbon corrosion, in the membrane, that occurs during the WE mode. It is important to note that the development of GO-Nafion composite membranes for URFC is not present in literature so the behavior of the composite membranes presented here should be deepen in term of different operating conditions, different catalyst loading and further modification of the membrane itself.



**Fig. 9.** Maximum power output over cycles (the cell operated with at 20 °C and atmospheric pressure in both electrolysis and fuel cell mode). Nafion was plotted with a black line, GO 0.5% with a red line, GO 1% with a blue line, GO 1.5% with a green line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Table 4**  
Power output over cycles of operation.

Membrane	Power output at first cycle [mW/cm <sup>2</sup> ]	Power output at last cycle [mW/cm <sup>2</sup> ]	Percentage deviation %
Nafion	43.75	36.75	-16
Nafion-GO (0.5%)	49.5	35	-29.3
Nafion-GO (1%)	31.875	22.5	-29.4
Nafion-GO (1.5%)	11.5	2.25	-80.4

**Table 5**  
Round trip efficiency.

Membrane	RT at first cycle [%]	RT last cycle [mW/cm <sup>2</sup> ]	Average RT
Nafion	29.5	22.2	26.6
Nafion-GO (0.5%)	31.7	19.4	26.1
Nafion-GO (1%)	21.9	11.1	16.4
Nafion-GO (1.5%)	7.5	1	3.8

#### CRediT authorship contribution statement

**Gabriele G. Gagliardi:** Writing – review & editing, Writing – original draft, Methodology, Data curation, Conceptualization. **Orlando Palone:** Writing – review & editing, Data curation. **Enrico Paris:** Methodology. **Domenico Borello:** Writing – review & editing, Supervision.

#### 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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