SELF-ASSEMBLING SULFONATED GRAPHENE OXIDE MEMBRANES FOR PEM FUEL CELLS

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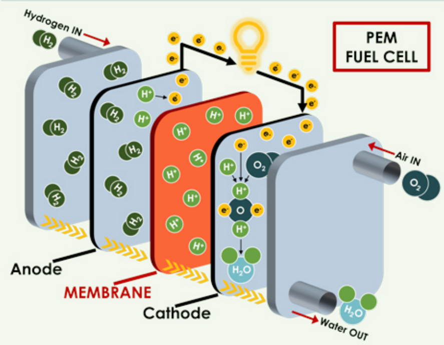
INTRODUCTION

A fuel cell **membrane** serves as **electrolyte** between anode and cathode. Therefore, it has to exhibit a rigorous set of properties, in the case of proton exchange membrane fuel cells [1]: high protonic conductivity; low permeability to H_2 and O_2 gases; electrical insulation; chemical, mechanical and thermal stability.

Even though **Nafion** is currently the most widely used electrolyte in PEMFC systems, some **drawbacks** induce the need of finding feasible replacements [2]: severe conductivity drop upon dehydration, limiting the possibility of fuel cell operation in conditions of high temperature and low humidity; swelling and shrinkage, leading the membrane to deteriorate at high water content.

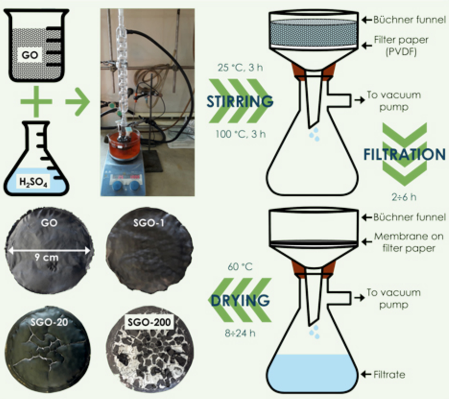


As shown in previous works, graphene oxide (GO) appears to be an excellent candidate for making both **FREESTANDING** [3] and hybrid membranes [4], thanks to its good mechanical properties and to the presence of oxygen-bearing functionalities that are likely to improve water retention. Its properties may also be enhanced by functionalization with some acid groups more tightly bound to its skeleton, e.g. sulfonic acid groups ($-SO_3H$) analogous to those of Nafion.

Hence, this work presents an effective method for the manufacturing of **SULFONATED GRAPHENE OXIDE (SGO)** membranes, which have been evaluated as a viable alternative to Nafion for operation at low relative humidity and high temperature.

MEMBRANES PREPARATION

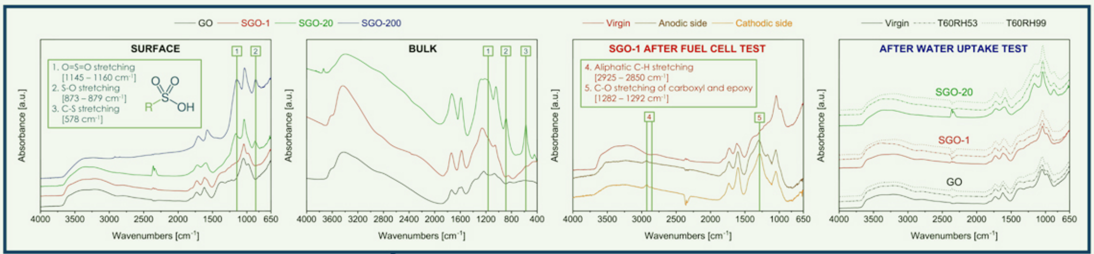
The original recipe [5] has been adapted by testing different **sulfonation ratios** (sulfuric acid-to-GO = 1; 20; 200), identified by making use of an **empirical formula** that has been derived from the elemental analysis of the commercial dispersion of graphene oxide: $C_{1.5}H_{0.2}N_{0.01}S_{0.03}O$.



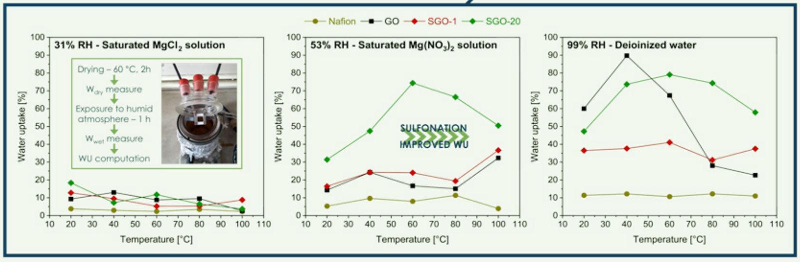
SAMPLE	ACID/GO MOLAR RATIO	THICKNESS [μm]	CONTACT ANGLE [°]
GO	0	13	69 ± 3.9
SGO-1	1	27	74.8 ± 2.7
SGO-20	20	76	76.7 ± 1.8
SGO-200	200	> 100	≈ 0

MEMBRANES CHARACTERIZATION

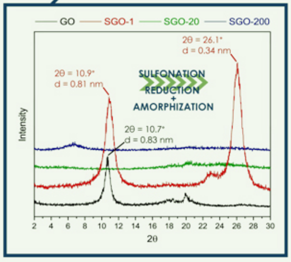
INFRARED SPECTROSCOPY (FTIR-ATR)



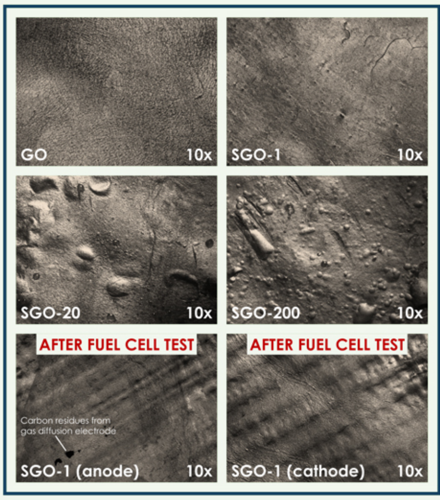
WATER UPTAKE BEHAVIOUR



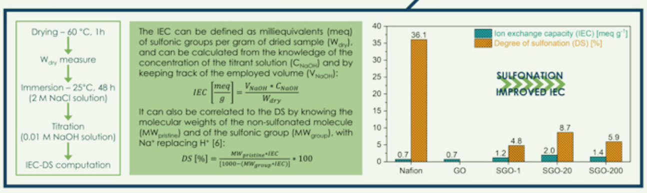
X-RAY DIFFRACTION



OPTICAL MICROSCOPY



IEC-DS EVALUATION

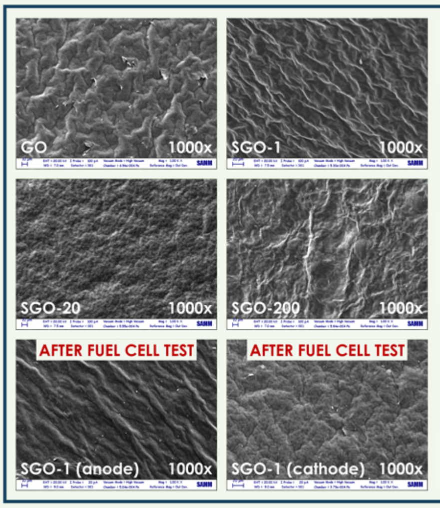


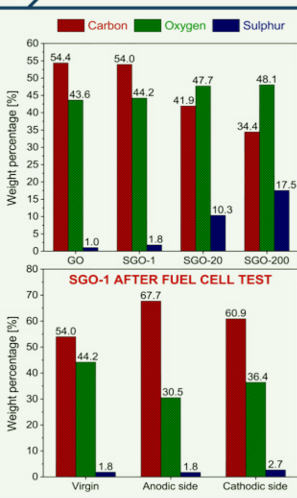
$$IEC\left[\frac{meq}{g}\right] = \frac{V_{NaOH} * C_{NaOH}}{W_{dry}}$$

$$DS\,[\%] = \frac{MW_{pristine} * IEC}{[1000 - (MW_{group} * IEC)]} * 100$$

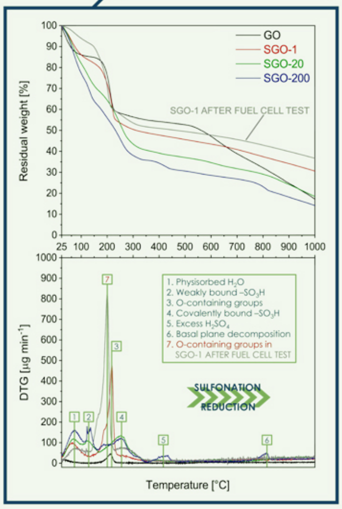
A preliminary test, carried out in a hydrogen-fed fuel cell on a sample of **SGO-1**, revealed a **promising mechanical resistance**, even though a low open circuit voltage has been measured (0.63 V) at 40 °C, due to possible hydrogen crossover issues. A subsequent examination of the active area at the optical microscope showed the sporadic presence of **carbon residues** left by the gas diffusion electrode (typical problem for Nafion), confirming a better resistance of SGO-1 to this kind of contamination. However, the results of FTIR-ATR and SEM-EDX analyses suggest that both anodic and cathodic surfaces of the membrane suffered **severe changes**, ascribed to the action of the fluxing gases.

SEM-EDX SPECTROSCOPY





THERMOGRAVIMETRY



CONCLUSION

- Functionalization proves to be stable after water uptake tests up to 60 °C
- Improvement in the water uptake behaviour at low T and RH, as well as in the ion exchange capacity, with respect to both pristine GO and Nafion
- Promising mechanical resistance in the fuel cell
- Reduction and amorphization of the SGO structure as a consequence of the functionalization process and of the fuel cell test

REFERENCES

[1] F. Barbir, PEM Fuel Cells: Theory and Practice, 2nd Ed., Academic Press, 2013
[2] Q. Li et al, Chem. Mater.,15, 4896 (2003)
[3] T. Bayer et al, J. Power Sources, 272, 239 (2014)
[4] M. Vinothkannan et al, Rsc Adv., 8, 7494 (2018)
[5] T. Cheng et al, Ionics (Kiel), 23, 2143 (2017)
[6] M. Kumari et al, J. Power Sources, 398, 137 (2018)

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