

# Innovative composite membranes based on PBI and GO/SGO as possible electrolytes for electrochemical devices

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## INTRODUCTION

The electrolytes employed in proton exchange membrane electrochemical devices (PEMEDs) should meet several requirements, such as good proton conductivity, low electronic conductivity, reduced permeability to gases, mechanical, thermal and chemical stability, and eventually a competitive price in order to favor a widespread commercialization<sup>1</sup>. Moreover, the ability to work at temperatures between 80 and 120 °C would allow a faster reaction kinetics, the use of less expensive electrocatalysts, and an easier water management. Therefore, the need of developing new materials able to outperform the conventional one, i.e., Nafion<sup>®</sup>, is becoming more and more urgent. In such a context, this work deals with the design of a simple, inexpensive, and reproducible method to fabricate innovative composite membranes in which polybenzimidazole (PBI) and graphene oxide (GO)/sulfonated graphene oxide (SGO) are combined. PBI proved remarkable thermal stability and workability<sup>2</sup>, whereas GO and its sulfonated derivative demonstrated a strong self-assembling tendency and a good proton conductivity, the latter of which is associated to their hydrophilic oxygenated functional groups<sup>3</sup>. Several PBI:(S)GO = X:Y mass ratios are studied, corresponding to GO/SGO mass contents one order of magnitude higher than the ones typically reported in literature<sup>4</sup>. The main goal is to investigate how the components influence the final properties of the produced stable self-standing membranes, besides verifying the possibility to use them as proton conductors.

## EXPERIMENTAL STUDY

The preparation of the PBI/GO and PBI/SGO composite membranes relied on the magnetic mixing under controlled conditions (1000 rpm, 1 hour, room temperature) of previously prepared 2 wt.% PBI-in-dimethyl sulfoxide (DMSO) and 1 wt.% GO/SGO-in-DMSO solutions, up to the obtainment of homogenous slurries. The slurries were then casted onto Petri dishes and oven-dried at 90 °C for a minimum of 3 hours, depending on the mass ratio of the membrane that was under production. The self-assembled membranes were recovered as intact products by simple detachment from the support. Then, the samples were characterized from the morphological and microstructural standpoint via scanning electron microscopy (SEM) and X-ray diffraction (XRD), from the thermal and mechanical standpoint via thermogravimetric analysis (TGA) and tensile tests (TT), while ion exchange capacity (IEC) evaluation and electrochemical impedance spectroscopy (EIS) tests were performed to evaluate the tendency towards proton exchange and transport of each composite membrane.

## RESULTS AND DISCUSSION

SEM images of the self-assembled composites highlighted the homogeneity of the prepared materials, likely related to an adequate reciprocal dispersion of the constituents at whichever mass ratio. As a consequence, the developed preparation procedure was regarded as reliable and easily reproducible. From XRD patterns, the formation of an alternated stacked framework was hypothesized, promoted by mutual  $\pi$ - $\pi$  interactions between the benzimidazole rings of PBI strands and the aromatic domains of GO flakes. Thermal stability of the samples below 130 °C was enhanced with respect to pure GO, due to the presence of PBI and the ability of the proposed alternated stacked structure to better trap moisture. Results from TT indicated higher tensile strengths and Young's moduli in the composites with respect to pure PBI, but at the cost of lower maximum strains, i.e., a sensible loss in plasticity. A clear increasing IEC trend up to values larger than virgin GO and Nafion<sup>®</sup> 212 was observed at higher GO mass contents, again recommending an optimal reciprocal dispersion of the two materials and the absence of PBI interference on the available proton exchange sites of GO. The extrapolated proton conductivities were promising, especially at 100 °C, thanks to the positive influence of the hydrophilic oxygenated functionalities of GO. On the contrary, lower values were obtained at 120 °C, probably due to a slight reduction of GO itself.

## CONCLUSION

A simple, cheap, and reliable route to prepare innovative PBI/GO and PBI/SGO composite membranes was developed. Characterization outcomes demonstrated the stability and uniformity of the composite membranes, the good interaction between the components, and promising IEC values and proton conductivities at high GO/SGO mass contents. The proposed materials were deemed worthy of further investigations to confirm their suitability as proton exchange membranes in PEMEDs.

## REFERENCES

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