Naphthalene Sulfonate-Functionalized Graphene Oxide Membranes as Potential Electrolytes for PEM Fuel Cells

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INTRODUCTION

The need of finding suitable replacements to Nafion® as the material of choice for the electrolyte of proton exchange membrane fuel cells (PEMFCs) was broadly addressed in recent research works[1], the main aim being to improve their performance at elevated temperature and low humidity. Among the investigated materials, graphene oxide (GO) and its sulfonated derivatives earned a significant interest from researchers, due to their remarkable self-assembling and proton-conducting properties, that make them an ideal candidate for the production of freestanding or composite membranes[2]. In this work we evaluated an innovative route to introduce sulfonic groups (-SO_3H) on the framework of GO, based on naphthalene sulfonate (NS) molecules. They were provided by Bozzetto Group (Filago, Bg, Italy) and were originally employed as a dispersing/fluidizing agent in polymerization processes. This study aims at producing freestanding naphthalene sulfonate-functionalized GO (NSGO) membranes with enhanced proton conductivity, in order to assess them as a potential electrolyte for PEMFCs. The proposed method can be considered in a perspective of circular economy and of valorization of these materials, which may possibly replace the expensive and complex sulfonation processes mostly performed nowadays[2].

EXPERIMENTAL/THEORETICAL STUDY

Membrane preparation was achieved by mixing in a round-bottomed flask an aqueous GO dispersion with controlled amounts of properly acidified NS powders. Three different GO-to-NS molar ratios were employed: 10:1 (10-NSGO), 5:1 (5-NSGO), 1:1 (1-NSGO). They were evaluated based on a tentative empirical formula of GO determined through the elemental analysis of the dispersion. For each molar ratio, two different procedures were implemented to assess the role of temperature on the functionalization reaction. In the former, the sulfonation of GO was carried out by stirring the mixture at 25 °C for 6 hours. In the latter, the dispersion was heated to 100 °C for the second half of the six-hour process. Afterwards, both kinds of solution were diluted with deionized water and vacuum filtered before drying the deposits in oven at 40 °C, so as to favor the self-assembling of the membranes. The so-obtained samples were characterized by optical microscopy, ATR-FTIR and SEM-EDX spectroscopies, TG-DTG analysis, XRD, static contact angle measurements and by the evaluation of their ion exchange capacity (IEC) and degree of sulfonation (DS). Then, the water uptake (WU) of selected specimens was tested at different temperatures and humidity values. Electrochemical impedance spectroscopy (EIS) allowed to evaluate their proton conductivity while their performance was assessed in a lab-scale hydrogen-fed fuel cell.

RESULTS AND DISCUSSION

The evidence of a successful functionalization of GO is observable in ATR-FTIR spectra, as bands that are compatible with the stretching vibrations of O=S=O (out of phase and in phase) and S-O bonds in sulfonic groups rise in the 1000-1250 cm^{-1} range. The bands that appear in the 730-850 cm^{-1} one may instead suggest the formation of C-S covalent bonds. The reaction temperature seems to affect the sulfonation effectiveness, as T100 specimens exhibit higher-intensity peaks in the abovementioned bands.

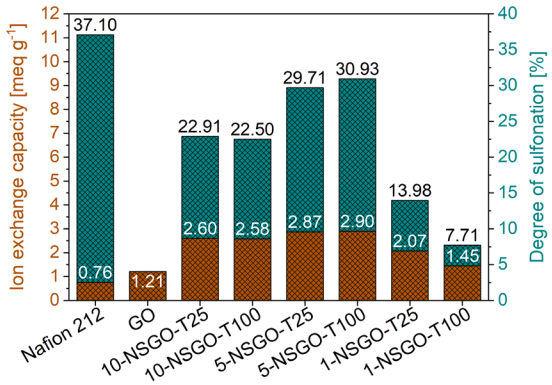

Fig. 1 IEC and DS of Nafion® 212, GO and NSGO.

SEM-EDX analyses confirm an increase in both sulfur and oxygen amounts of NSGO membranes with respect to pure GO ones, as expected from the different NS content. The IEC is largely improved in sulfonated membranes (Fig. 1), but it does not follow the molar ratio trend, as 1-NSGO ones show the lower results despite the higher quantity of sulfonating agent. A possible reason is that the trapping of an excess of unreacted powders in the final product hinders an efficient proton exchange. WU, EIS and fuel cell tests contribute to validate both functionalization efficacy and promising performance of NSGO membranes.

CONCLUSION

An innovative and simple way to accomplish an effective sulfonation of GO has been proposed. Characterization results seem to certify the promising nature of the obtained membranes for a possible application as the electrolyte material for PEMFCs.

REFERENCES

1. J. Park et. al, Curr. Opin. Electrochem. 5, 43 (2017)
2. R. Pandey et. al, Adv. Colloid Interfac. 240, 15 (2017)