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GRAPHENE OXIDE-BASED COMPOSITE MEMBRANES AS NOVEL ELECTROLYTES FOR PEM FUEL CELLS

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***Abstract* – A novel approach is presented for the production of self-assembling sulfonated graphene oxide membranes, with the aim of evaluating them as an alternative to Nafion® for the application in PEMFCs as proton-conducting electrolytes. The functionalization has been performed by reacting a commercial aqueous dispersion of graphene oxide (GO) with different volumes of sulfuric acid, studying their effect on both structure and degree of sulfonation of the membranes. The specimens have been characterized from the morphological viewpoint by ATR-FTIR, XRD and SEM-EDX spectroscopies, thermogravimetric analysis, optical microscopy and static contact angle measurements. Their water uptake, ion exchange capacity and degree of sulfonation have been evaluated as well, and the relationship among them allowed the identification of an optimal acid-to-GO molar ratio for the sulfonation reaction. These tests resulted in an improved behavior compared to both Nafion® and pristine GO, while promising results have been obtained from a preliminary fuel cell test.**

***Index Terms* – Electrolyte, graphene oxide, PEM fuel cells, sulfonation.**

I. NOMENCLATURE

SGO-X: sulfonated graphene oxide membranes prepared with an acid-to-GO molar ratio equal to X (1, 20 or 200).

II. INTRODUCTION

One of the fundamental components of proton exchange membrane fuel cells (PEMFCs) is the proton-conducting electrolyte, nowadays commonly based on Nafion®, a perfluorosulfonate ionomer produced by DuPont. This membrane material is characterized by hydrophilic lateral substituents containing sulfonic acid groups ($–SO_3H$), which are responsible for its high proton conductivity (> 0.1 S cm^{-1}) under humidified conditions. However, Nafion® is expensive and suffers both a rapid performance drop and a physical degradation at low relative humidity (< 50%) and elevated temperatures (> 80 °C). Therefore, huge research efforts have been deployed for the development of new materials able to operate at such conditions, which would significantly enhance both kinetics and efficiency of the redox reaction, while simplifying water management and cell design [1,2].

Among the possible approaches, graphene oxide (GO) has gained a lot of interest because of the presence of several oxygenated functionalities, which are responsible for the self-assembling properties that make it an ideal candidate for the production of freestanding membranes. However, previous works displayed a poor performance and durability of GO-based electrolytes [3]. Thus, the aim of this work has been to improve the properties of GO by exploiting an innovative approach consisting in its functionalization with sulfonic acid groups analogous to those of Nafion®. The obtained membranes have been extensively characterized from both morphological and operative points of view, providing promising results.

III. MEMBRANES PRODUCTION

The sulfonation of GO has been performed by developing a reaction between sulfuric acid and a commercial water-based dispersion of GO (4 mg mL^{-1}) acquired from Graphenea. Three tentative acid volumes have been defined according to a sulfonation procedure proposed in literature [4], and they correspond to three different acid-to-GO molar ratios (1, 20 and 200). The latter have been calculated by considering a structural

formula of GO ($C_{1.5}H_{0.2}N_{0.01}S_{0.03}O$), which has been roughly estimated from the elemental analysis of the commercial dispersion.

IV. MORPHOLOGICAL AND OPERATIVE CHARACTERIZATION

The effectiveness of the proposed sulfonation method has been confirmed by ATR-FTIR and SEM-EDX spectroscopies. The latter demonstrated an increase in the weight percentages of oxygen and sulfur after the functionalization reaction, while the former allowed to identify the characteristic bands corresponding to the stretching vibrations of O=S=O (1143-1153 cm^{-1}) and S–O (870-880 cm^{-1}) in sulfonic acid groups, as displayed in Fig. 1. In addition, with respect to the infrared spectrum of virgin GO, in those of SGO membranes we witnessed the vanishing of the bands corresponding to carboxyl moieties (1300-1400 cm^{-1}) and to less stable oxygenated functions (981 cm^{-1}), such as lactols and peroxides. Along with the appearance of the stretching mode (1580 cm^{-1}) of C=C bonds in sp^2, unoxidized, graphitic domains, this suggested that the functionalization reaction has induced a probable reduction and amorphization of the structure of GO. These findings have been verified by X-ray diffraction and thermogravimetric analyses as well.

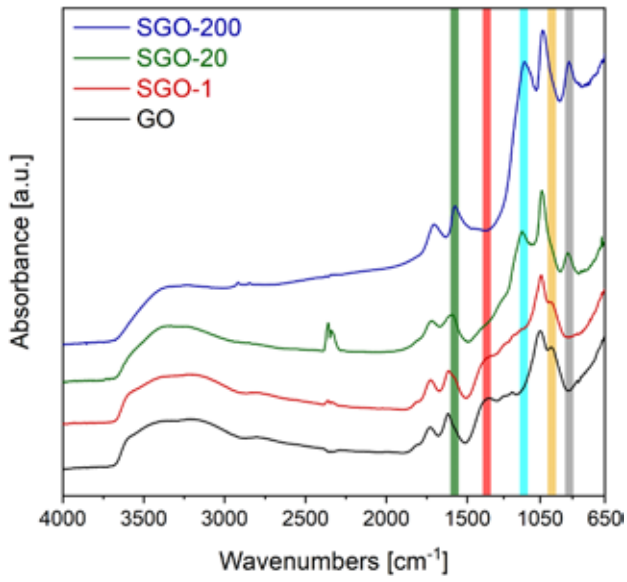

Fig. 1. ATR.FTIR spectra of GO and SGO-X membranes; colored bands point out the characteristic vibrations of S–O (gray), O=S=O (cyan) and C=C (green) bonds, as well as those of carboxyl (red) and less stable (yellow) moieties that are lost after sulfonation.

Water uptake tests have been carried out in a small-scale humid chamber by exploiting an oil bath to control the temperature between 20 and 100 °C, while deionized water or a saturated solution of $Mg(NO_3)_2$ have been employed to vary the level of humidification between 95% and 53%, respectively. Sulfonation resulted in an improved water uptake behavior as against both virgin GO and Nafion®, in particular at reduced humidification and elevated temperature. However, the rising of the acid-to-GO molar ratio caused a significant increase in the swelling ratio, symptom of a reduced structural stability. The ion exchange capacity has been enhanced as well by the functionalization with sulfonic acid moieties, with values higher than 1 meq g^{-1} for SGO-X membranes, almost twice the one measured for a reference sample of Nafion® 212 (about 0.7 meq g^{-1}). The best results have been achieved with X = 20, suggesting that the optimal sulfonation ratio probably lies close to this value.

The preliminary test in a hydrogen-fed fuel cell performed on a specimen of SGO-1 demonstrated a promising compression resistance and a practically absent contamination by carbon residues coming from the gas diffusion electrode, which are a typical issue in the case of Nafion and a sign of degradation of the catalyst. The open circuit voltage has been significantly improved with respect to virgin GO (0.63 vs 0.24 V), but it is still too low for practical applications, most likely because of hydrogen crossover issues. However, morphological and thermal characterization performed after the test demonstrated a fair stability of the functionalization to the fuel cell environment, especially in the bulk, while major changes took place on the surface, with the loss of less stable moieties.

V. CONCLUSION

A simple and effective method has been developed for the sulfonation of graphene oxide, and the resulting membranes have shown a promising behavior under different testing conditions, in particular from the point of view of water uptake and ion exchange capacity. These results confirmed the potential of freestanding sulfonated graphene oxide for the application in PEMFCs as an alternative electrolyte to Nafion®. Future developments of these components should address some stability issues concerning the introduced functionalities, in order to make the sulfonation process more efficient and to improve the cohesion of the membrane.

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