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Sulfonated graphene oxide as innovative self-assembling electrolyte for PEM fuel cells

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Sulfonated graphene oxide (SGO) membranes have been developed and evaluated as a viable alternative to Nafion® in polymer electrolyte membrane fuel cells (PEMFCs). Even though Nafion® is currently the most widely used electrolyte in PEMFC systems, some crippling drawbacks induce the need of finding feasible replacements. In particular, Nafion® suffers a severe conductivity drop upon dehydration, which limits the possibility of operation in conditions of high temperature and low relative humidity [1]. As shown in previous works, graphene oxide (GO) appears to be an excellent candidate for making both freestanding [2] and polymer-based hybrid membranes [3], thanks to its good mechanical properties and to the presence of oxygen-containing functionalities that are likely to improve water retention. However, we verified in a preliminary study [4] that, at high temperatures, GO suffers a partial loss of the chemical groups which foster protons transport and a lowering of the structural integrity of the carbon network. Hence, its properties may 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®.

In this work, we present an effective method for the sulfonation of graphene oxide, based on the reaction between sulfuric acid and a commercial aqueous dispersion of GO. Different samples have been prepared by varying the quantity of sulfuric acid employed in the sulfonation reaction, and an optimal acid-to-GO molar ratio has been identified, taking into account an empirical formula of GO. Such formula has been derived, as a first approximation, from the elemental analysis of the commercial solution and confirmed by the results of SEM and EDX analysis. The sulfonated membranes have been widely characterized by ATR-FTIR, XRD, SEM and EDX spectroscopies, thermogravimetric (TG-DTG) analysis, optical microscopy and static contact angle (OCA) measurements. These techniques confirmed the effective functionalization of GO and the stability of sulfonic acid groups even after water uptake (WU) experiments, which have been carried out at different temperatures and relative humidity. The ion exchange capacity (IEC) of the different samples has been evaluated as well, and a correlation among WU, IEC and degree of sulfonation (DS) can be established. Test results showed that sulfonated membranes have an improved WU behaviour with respect to both Nafion and unfunctionalized GO, especially at low temperature and humidity (**Fig. 1**); they also show an IEC value higher than 1 meq/g, which is even better than IEC determinations reported for Nafion® [5]. The increase of the amount of sulfuric acid seems to be beneficial for both properties. Then, one sulfonated membrane has been selected and subjected to a preliminary test in a lab-scale hydrogen-fed fuel cell. Promising results have been found from the point of view of mechanical resistance, even though a low open circuit voltage (OCV) has been measured (0.63 V) at 40 °C, which might be ascribed to hydrogen crossover issues. These issues should be addressed in future developments of such components. However, after testing, the active area showed absence of carbon residues left by the gas diffusion electrode (GDE), which are a typical problem in the case of Nafion®.

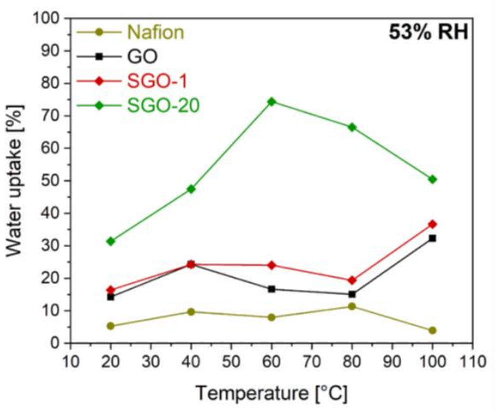

Fig. 1. WU as a function of temperature at 53 % relative humidity. Two different acid-to-GO molar ratios are reported.

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