

Borate-Reinforced Sulfonated Graphene Oxide Membranes as an Alternative Proton Conductor for PEM Fuel Cells

Andrea Basso Peressut ^{1*}, Saverio Latorrata ¹, Paola Gallo Stampino ¹ and Giovanni Dotelli ¹

¹Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Italy

*andreastefano.basso@polimi.it

INTRODUCTION

Graphene oxide (GO) and its sulfonated versions (SGO), bearing sulfonic groups (-SO₃H), have been extensively studied by researchers to be used as a potential alternative to Nafion[®] as the electrolyte of proton exchange membrane fuel cells (PEMFCs). Their main point of interest is the combination of a noteworthy proton conductivity with an excellent self-assembling ability, enabling the production of freestanding membranes^{1,2}. Nevertheless, issues of poor structural stability have emerged, in spite of the excellent mechanical properties of the individual flakes, because they are kept together by weak hydrogen-bonding and van der Waals interactions, which reduce the overall strength. A possible remedy to this flaw, borrowed from nature, is the exploitation of borate ions to improve the cohesion of the membrane, as they might promote the linkage among the oxygenated groups of different GO sheets³. Therefore, this work proposes an effective method to manufacture standalone borate-reinforced membranes (SGO+B), based on a GO matrix adequately functionalized by both sulfonic acid groups and sodium tetraborate decahydrate, with the aim of enhancing their proton-conducting properties and structural stability.

EXPERIMENTAL/THEORETICAL STUDY

The borate-modified membranes were produced starting from a commercial aqueous dispersion of GO (4 mg mL⁻¹, Graphenea Inc.), 25 mL of which were put into a round-bottomed flask and underwent 10 min of a mild ultrasound bath. Sulfonation was carried out after sonication by introducing precise amounts of sulfuric acid, in order to achieve different acid-to-GO molar ratios. The mixture was then subjected to 6 h of magnetic stirring at 50 °C, in order to favor the sulfonation reaction. Afterwards, it was diluted with deionized water to a concentration of 0.75 mg mL⁻¹ and mixed under vigorous stirring to controlled volumes of a 0.1 M solution of sodium tetraborate decahydrate³. The resulting dispersion was then vacuum filtered on a PVDF filter and dried in oven, so as to remove the excess of water and to favor the formation of the expected borate-mediated bonds among the GO sheets. Reference membranes with no sulfonation (GO+B), no borate addition (SGO) or neither of them (GO) were prepared as well as a basis for comparison. The previous samples were characterized by employing ATR-FTIR and SEM-EDX spectroscopies, TG-DTG and static contact angle analyses, XRD, and by measuring their ion exchange capacity (IEC) and degree of sulfonation. Selected samples underwent water uptake tests at different conditions of temperature and humidity, while

their proton conductivity was assessed by electrochemical impedance spectroscopy. A preliminary evaluation of their performance was eventually conducted in a lab-scale hydrogen-fed fuel cell.

RESULTS AND DISCUSSION

The main aim of the applied characterization procedures was to evaluate the successful introduction of both sulfonic acid and borate-based groups into the membranes, as well as to assess their practical performance, in view of their possible application as an electrolyte in PEMFCs. The effectiveness of the sulfonation reaction is demonstrated in ATR-FTIR spectra by the rising of bands that can be ascribed to the stretching vibrations of O=S=O and S-O bonds in -SO₃H groups. These results are also in agreement with those of SEM-EDX spectra, displaying an increase in the contents of oxygen and sulfur with respect to bare GO. The effect of borate functionalization seems clearer in non-sulfonated (GO+B) membranes, whose ATR-FTIR spectra exhibit a reduction in C-OH and O-H signals referred to hydroxyl and carboxyl groups. This is a potential symptom of the formation of interplanar bonds among the oxygen-bearing functions of different GO layers³. Then, GO+B membranes also exhibit a higher thermal stability in the typical operating range of PEMFCs, as witnessed from TG-DTG analyses. On the other hand, the consequences of borate addition are of less clear interpretation in the case of SGO+B specimens, because there might be a competition between -SO₃H and borate groups in substituting GO's functionalities. However, these samples seem to exhibit a superior swelling resistance compared to both Nafion[®] 212 and pristine GO, while keeping a good water sorption. This may result in a higher resistance to mechanical degradation caused by wet/dry cycles during cell operation. In addition, the presence of borates seems to influence positively the value of the IEC, which is improved as against Nafion[®] 212, GO and SGO samples.

CONCLUSION

We presented a straightforward and efficient procedure to fabricate self-standing, borate-treated SGO membranes, whose characterization evidenced a promising structural stability coupled to a fair proton conductivity, which make them an interesting candidate for a successful application as a novel electrolyte for PEMFCs.

REFERENCES

1. T. Bayer et. al, *J. Power Sources* 272, 239 (2014)
2. R. Kumar et al, *Chem. Commun.* 48, 5584 (2012)
3. Z. An et al, *Adv. Mater.* 23, 3842 (2011)