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Enhancing Proton Conductivity of SPEEK Based Membranes by Incorporation Graphene Oxide / Bisphosphonic acid dopant

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INTRODUCTION

The most commercially successful membrane for applications in fuel cell and electrolyzers, perfluorinated sulfonic Nafion^{R}, exhibits relevant performance limitations due to its dependence on water content with consequent proton mobility restrictions, environmental concerns and very high cost. Poly(etheretherketone) (SPEEK) polymer appears as a versatile non-fluorinated alternative for a low-cost and a more environmentally friendly membrane. Our previous studies showed that the incorporation of biphosphonic acid dopants (BPs) into the mentioned polymeric matrices, improves membrane proton conduction and durability[1-5]. In this work, we prepared and evaluated new doped SPEEK membranes using graphene oxide (GO) with bisphosphonic acid functionalities as dopant (GOBP), anticipating superior membranes properties, including proton conductivity.

EXPERIMENTAL

GOBP dopant was prepared by phosphorylation reaction with PCl_3 in water, at 65 ºC, from GO (GO-COOH, Nanoinnova Technologies SL)[6]. SPEEK polymer was made by sulfonation of PEEK with sulfuric acid[5] and was characterized by NMR and ATR-FTIR. Membranes, with 64% sulfonation degree, were cast from a SPEEK/DMF solution with 0.5, 1.0 or 2.0 wt% of GOBP dopant which was characterized by ATR-FTIR. The new SPEEK doped membranes were analyzed by SEM, TGA and ATR-FTIR spectroscopy. Proton conductivity was evaluated by electrochemical impedance spectroscopy (EIS) from 30 to 60 ºC, under 100% RH conditions, using a Solartron FRA coupled to an electrochemical interface and a BekkTech conductivity cell.

RESULTS

Doped membranes were casted with different wt% loadings of GOBP and further analyzed by different analytical techniques to assess the presence of functional groups, integrity and homogeneity of the surface, and thermal stability, with positive results. The incorporation of GOBP into SPEEK membranes, at all studied loads, shows an increase in the proton conduction with temperature, and better performances relative to the pristine membrane, with the highest value of 240 mS cm^{-1}, observed at 60 ºC for 1.0 wt% dopant load. Activation energy values were also estimated.

CONCLUSION

New GOBP doped SPEEK membranes have been successfully prepared and their properties evaluated with positive results. The devised strategy integrates research in progress to explore the dopant effect on the performance and durability of membranes at higher temperatures for applications in HT-PEMFCs, extending the range of properties to stability under oxidative conditions, mechanical stability, and resistance to gas crossovers.

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