

Sulfonated Graphene Oxide as Alternative Proton Conductor for PEM Fuel Cells

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INTRODUCTION

In this work a simple method for preparing sulfonated graphene oxide (SGO) membranes which are intended to be used as a potential alternative electrolyte for proton exchange membrane fuel cells (PEMFCs) is reported. The need to develop a new generation of electrolytes stems from the awareness of the drawbacks exhibited by Nafion which limits fuel cell maximum operating temperature since its conductivity dramatically decreases upon dehydration¹. Therefore, it would be desirable to find a feasible alternative for operations at high temperature and low humidity. Among the possible approaches, graphene oxide (GO) has gained interest for the production of both self-standing membranes and hybrid composites². Indeed, GO seems to be a superb candidate as a novel electrolyte for PEMFCs due to its self-assembling and mechanical properties together with the presence of oxygen-containing hydrophilic functional groups which might improve water retention and lead to a more efficient proton conduction. Actually, in previous studies pristine GO membranes have shown some problematic aspects such as high crossover losses, unsatisfactory durability and partial loss of proton-conducting groups at high temperature³. Hence, in order to enhance its mechanical and conduction properties, GO needs to be functionalized with different acid groups more tightly bound to its layers. In a recent preliminary work³, we explored the feasibility of an easy method to introduce, into the GO structure, sulfonic acid groups (-SO₃H). In the present work we identified an optimal sulfuric acid to GO ratio on the basis of a precise formula for GO determined from elemental analysis of the employed commercial dispersion.

EXPERIMENTAL/THEORETICAL STUDY

In a typical experiment, the GO dispersion was mixed with variable contents of sulfuric acid; on the basis of elemental analysis of the commercial GO dispersion employed, a tentative empirical formula was determined, and it allowed to calculate the molar ratio between GO and sulfuric acid. After 3 hours, the solution was transferred into a round-bottomed flask and heated to 100 °C under stirring (650 rpm) in order to favor the sulfonation reaction. The solution was then washed with deionized water to neutral, vacuum filtered and the so-obtained membrane dried for 24 hours at 80 °C. Uniform and self-assembled membranes were obtained and characterized by ATR-FTIR spectroscopy, TG-DTG analysis, XRD, SEM and EDX spectroscopy. Then, water uptake and ion exchange capacity (IEC) as a function of

both temperature and relative humidity were measured; degree of sulfonation was calculated accordingly. Impedance spectroscopy was also performed in order to assess proton conductivity.

RESULTS AND DISCUSSION

The successful sulfonation of GO is confirmed by ATR-FTIR spectroscopy. New peaks appear in the spectra of sulfonated membranes, compatible with the S-O (870-880 cm⁻¹) and O=S=O (1145-1165 cm⁻¹) stretching vibrations of -SO₃H groups.

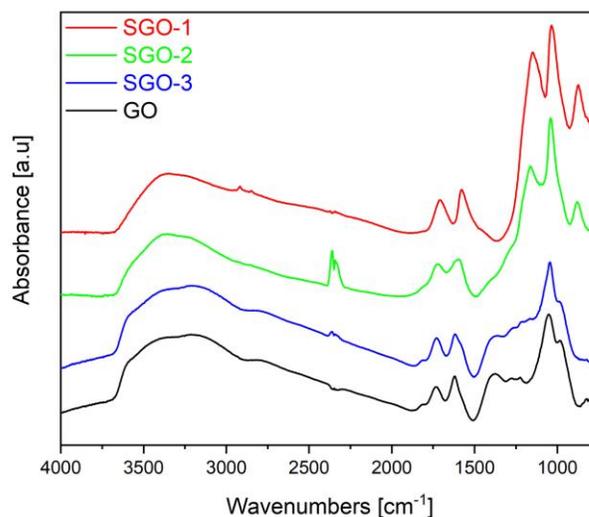


Fig. 1 ATR-FTIR spectra of GO and SGO samples.

Functionalization becomes more effective by increasing the amount of sulfuric acid (SGO-3 < SGO-2 < SGO-1), as confirmed by EDX spectroscopy as well, with an increase in the content of sulphur and oxygen with respect to pristine GO. ATR-FTIR spectra also show that functional groups are retained after water uptake tests, confirming the stability of the membranes. Sulfonated samples also display improved water uptake (especially at low relative humidity) and IEC with respect to GO.

CONCLUSION

The sulfonation of GO has been demonstrated with a simple and effective method, which seems promising for the production of an innovative electrolyte for PEMFCs.

REFERENCES

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