

# Proton conductivity of Nafion-azolebisphosphonates membranes for PEM fuel cells

Fátima C. Teixeira<sup>1</sup>, Ana I. de Sá<sup>1</sup>, António P. S. Teixeira<sup>2</sup> and Carmen M. Rangel<sup>1</sup>

<sup>1</sup>Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal.

<sup>2</sup>Departamento de Química, Escola de Ciências e Tecnologia & Centro de Química de Évora, IIFA, Universidade de Évora, R. Romão Ramalho, 59, 7000-671 Évora, Portugal

email: carmen.rangel@lneg.pt

## INTRODUCTION

Energy systems with cleaner and sustainable sources are crucial challenges of the 21st century to deal with the environmental threat of global warming and the declining reserves of fossil fuels. Fuel cells are electrochemical devices that convert the chemical energy stored in a fuel directly into electrical energy, providing electrical energy with high efficiency and low environmental impact. Among them, proton exchange membrane fuel cells (PEMFCs) are considered promising power sources, due to their high power density and high power-to-weight ratio but their performance depends crucially on their proton exchange membranes [1]. Usually, these membranes are made of organic polymers containing acidic functionalities (ex. Nafion<sup>®</sup>), which proton transport properties strongly depend on their water content and, consequently, limit their operation temperatures up to 90°C. Preliminary studies have demonstrated that incorporation of aryl-bisphosphonic acids into Nafion, by casting, results in an enhancement of the proton conductivity of the membrane.

The aim of this work was the preparation of new Nafion membranes doped with azolebisphosphonates derivatives, which could act as a source of protons and also function as proton acceptors, facilitating the intermolecular transmission of protons through the membrane.

## EXPERIMENTAL

Azolebisphosphonic acids (BPs) were synthesized in several steps following modification of procedures already described by the authors [2]. Membranes were prepared by casting Nafion<sup>®</sup>/DMAc solutions with 1.0% wt. of azoleBP dopants. Dopants were characterized by spectroscopic methods (NMR, FTIR, MS). Nafion membranes were submitted to ATR FT-IR spectroscopy analysis. The proton conductivity of the new membranes was obtained from electrochemical impedance spectroscopy (EIS) spectra, acquired with a frequency response analyzer coupled to an electrochemical interface from Solartron. The measurements were carried out in a BekkTech conductivity cell located in a climate chamber and varying the temperature (30-60°C) and the relative humidity (RH, 40-80%).

## RESULTS AND DISCUSSION

In order to prepare the indazole- and benzotriazoleBPs (Fig. 1), several strategies were followed with different

kind of reagents. The spectroscopic characterization allowed the assignment of regioisomers **BP3** and **BP4**.

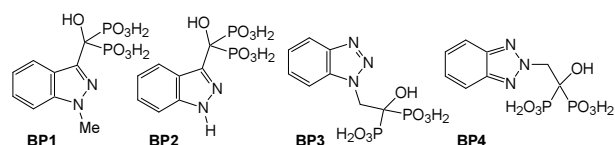


Fig. 1. AzoleBPs used as dopants

Proton conductivity studies were performed for membranes doped with azoleBPs at different temperatures and RH. The proton conductivity of all membranes increases with the increasing of the temperature and the RH (Fig. 2). All prepared membranes show higher proton conductivity than Nafion N-115.

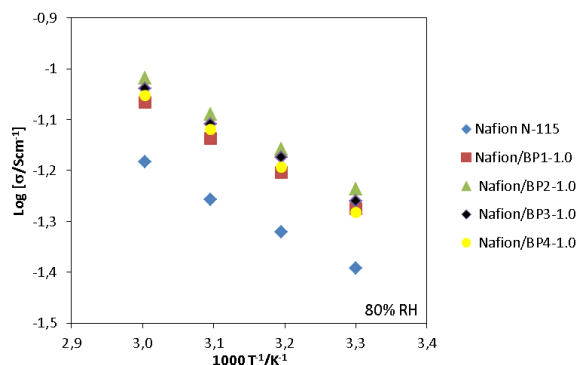


Fig. 2. Proton conductivity of Nafion and Nafion modified membranes vs reciprocal temperature at 80% RH.

## CONCLUSION

New doped membranes showed higher proton conductivity than Nafion. The presence of azoleBPs in Nafion membranes enhances the proton conductivity of all membranes, showing higher values with the increasing of temperature and RH. These results show a promising approach to obtain membranes for PEMFC.

## REFERENCES

1. H. Zhang et al., Chem. Soc. Rev. 41, 2382 (2012).
2. F. Teixeira et al., Heteroatom Chem. 26, 236 (2015).

## ACKNOWLEDGMENTS

This research was supported by the Project “PEMFC-SUDOE” - SOE1/P1/E0293 which is co-financed by the European Regional Development Fund in the framework of the INTERREG SUDOE programme.