New Proton Conductive Heteroaromatic Bisphosphonic acid-Nafion Membranes for PEMFC

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INTRODUCTION

The integration of new cleaner, renewable and environment-friendly sources and energy vectors for sustainable energy systems are a key challenge for 21st century society[1]. Fuel cells are among the clean energy conversion technologies with vast applications and scope, introducing hydrogen as a flexible and storable energy vector and presenting a viable alternative to fossil fuels. Proton exchange membrane fuel cells (PEMFCs) are considered promising power sources, but their performance depends crucially on the properties of their proton exchange membranes (PEM). These membranes strongly depend on the presence of conducting water or other electrolyte content, which limits their operation to 80 ºC[2].

In order to advance novel membranes for application in PEMFCs, we have developed a series of bisphosphonic acid derivatives, which are used as dopants. Herein, we present the preparation and characterization of the new Nafion doped membranes, and the evaluation of their proton conductivity at different temperature and relative humidity (RH) conditions.

EXPERIMENTAL/THEORETICAL STUDY

Indazole and condensed pyrazole bisphosphonic acids (BPs) were synthesized following modified experimental procedures[3] and were characterized by spectroscopic methods (NMR, FTIR, MS). Membranes were prepared by casting Nafion®/DMAc solutions with 1.0 wt% of BP dopants. Nafion membranes were submitted to ATR-FTIR spectroscopy analysis and SEM. Ion Exchange Capacity (IEC) of new membranes was obtained by potentiometric titration, and their water uptake was determined by gravimetric tests. Proton conductivity of the membranes was evaluated by electrochemical impedance spectroscopy (EIS). The measurements were performed inside a climate chamber, as a function of temperature and relative humidity (RH).

RESULTS AND DISCUSSION

Indazole and condensed pyrazole bisphosphonic acids (Fig. 1) were synthesized using strategies devised by us on previous studies[3]. The spectroscopic characterization allowed the assignment of their structure.

New Nafion membranes, doped with BPs (Fig. 1), were successfully prepared by casting and were characterized. Studies of IEC and water uptake of new membranes showed higher values than Nafion, revealing that the incorporation of dopants turns the membranes more hydrophilic, with higher proton content.

Their in-plane proton conductivity showed an increment with the increasing of temperature (30-60 ºC) and RH conditions (40-80%) (Fig. 1), indicating that these conditions are important in the proton transport. All membranes showed higher proton conductivities than Nafion, with values up to 60% higher, when tested in the same experimental conditions, suggesting that these Nafion-doped membranes are good candidates to obtain membranes with better proton conductivity.

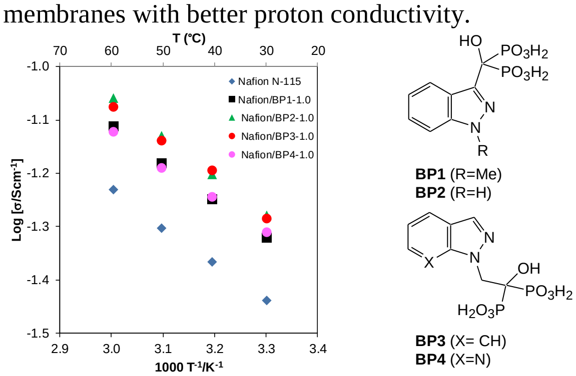

Fig. 1. Arrhenius plots for in-plane proton conductivity of new Nafion-bisphosphonic acids membranes

The activation energy (Ea), required for the proton transport throughout the membranes, were estimated using the Arrhenius equation, indicating that both vehicular and Grotthuss mechanisms coexist under the studied conditions.

CONCLUSIONS

New Nafion doped membranes were prepared and their proton conductivity were evaluated. The incorporation of BPs dopants on Nafion polymer enhances the proton conductivities of the new membranes, with all membranes showing higher proton conductivities than Nafion.

REFERENCES

1. S. Guo et al., Renew. Sustain. Energy Rev. 91, 1121 (2018).
2. A. Kusoglu et al., Chem. Rev. 117, 987 (2017).
3. F.C. Teixeira et al., Heteroat. Chem. 26, 236 (2015).

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