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New proton conductive membranes of indazole- and condensed pyrazolebisphosphonic acid-Nafion membranes for PEMFC

Fátima C. Teixeira[1], António P. S. Teixeira[2] and Carmen M. Rangel[1]

[1] *Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal*

[2] *Departamento de Ciências Médicas e da Saúde, ESDH & LAQV- REQUIMTE, IIFA, Universidade de Évora, R. Romão Ramalho, 59, 7000-671 Évora, Portugal*

carmen.rangel@lneg.pt

The global demands of energy are still increasing alongside many civilizational problems, notably the effects on the environment due to the overuse of traditional energy sources based on fossil fuels. New cleaner, renewable sources for sustainable energy systems are a key challenge of the 21st century society. There is a societal effort towards the use of renewable energies, but the actual sources remain low density, unstable and intermittent production providers [1]. Fuel cells are among the clean energy conversion technologies, that using hydrogen, can provide electrical energy with high efficiency and low environmental impact. Membranes for proton-exchange membrane fuel cells (PEMFC) still are a key component for this technology [2].

Our previous studies have demonstrated that incorporation of dopants into Nafion results in an enhancement of their proton conductivity [3-5]. Following our long-standing interest on PEMFC membranes, the aim of this work centers on the preparation of new Nafion membranes doped with azaheteroaromatic bisphosphonic acid (AzBPs) derivatives. These AzBPs are expected to act both as a source of protons and proton acceptors, facilitating the intermolecular transmission of protons throughout the membrane.

In this study, we report on different AzBPs derivatives (Figure 1(a)), following strategies devised on our previous studies, to afford two indazole-bisphosphononic acid substituted at N-1 with a side chain of one or two methylene groups, and pyrazolo[3,4-*b*]pyridine- and pyrazolo[3,4-*b*]quinolinebisphosphononic acid substituted at N-1.

New doped Nafion membranes were prepared by casting with 1 wt% loading of the prepared AzBPs. The new membranes were analysed by ATR-FTIR spectroscopy and their morphology was examined by SEM. The new membranes were evaluated for their water uptake capacity, by gravimetry, their ion exchange capacity (IEC), by determining the presence of ionizable groups on the membrane through an acid-base potentiometric titration, and their degree of hydration. The proton conduction properties were evaluated by Electrochemical Impedance Spectroscopy (EIS). The in-plane proton conductivity of the membranes doped with AzBPs were evaluated at different temperatures (30, 40, 50 and 60 ºC) and RH conditions (40, 60 and 80%). The proton conductivity of all membranes increases with the increasing of temperature and RH (Figure 1(b)).

The incorporation of AzBPs dopants on Nafion polymer enhances the proton conductivities since all prepared membranes show higher proton conductivities than Nafion N-115, used as a reference, with values up to 1.42-fold, when tested in the same experimental conditions. In the studied conditions, all new membranes exhibited proton conductivities of the same order of magnitude. The best proton conductivity was observed for membrane doped with **AzBP1** as dopant, with a value of 94 $mScm^{-1}$. These results indicate that the azaheteroaromatic bisphosphonic acid-Nafion doping is a promising approach to obtain new membranes for PEMFC with better proton conductivity.

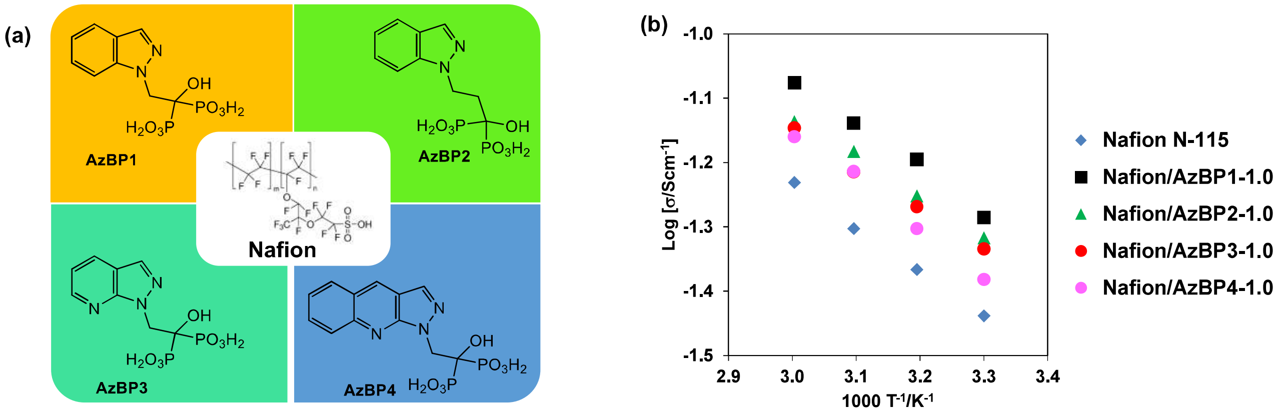

Figure 1: (a) AzBPs used as dopants of Nafion; (b) Proton conductivity of Nafion membranes vs reciprocal temperature at 80% RH.

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References
[1] I. Staffell, D. Scamman, A.V. Abad, P. Balcombe, P.E. Dodds, P. Ekins, N. Shahd, K.R. Ward, "The role of hydrogen and fuel cells in the global energy system", Energy Environ. Sci., 12, 2019, 463-491.
[2] A. Kusoglu, A.Z. Weber, "New insights into perfluorinated sulfonic-acid ionomers", Chem. Rev., 117, 2017, 987-1104.
[3] F.C. Teixeira, A.I. de Sá, A.P.S. Teixeira, C.M. Rangel, "Nafion phosphonic acid composite membranes for proton exchange membrane fuel cells", Appl. Surf. Sci., 487, 2019, 889-897.
[4] F.C. Teixeira, A.I. de Sá, A.P.S. Teixeira, C.M. Rangel, "Enhanced proton conductivity of Nafion-azolebisphosphonates membranes for PEM fuel cells", New J. Chem., 43, 2019, 15249-15257.
[5] F.C. Teixeira, A.I. de Sá, A.P.S. Teixeira, V.M. Ortiz-Martinez, A. Ortiz, I. Ortiz, C.M. Rangel, "New modified Nafion-bisphosphonic acid composite membranes for enhanced proton conductivity and PEMFC performance", Int. J. Hydrogen Energy, 46, 2021, 17562-17571.