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Enhanced proton conductivity of Nafion-azolebisphosphonate membranes for PEM fuel cells

Fátima C. Teixeira,[a] Ana I. de Sá,[a] António P. S. Teixeira[b] and C. M. Rangel *[a]

Fuel cells are among the cleaner alternatives of sustainable energy technologies, where their proton exchange membranes continue to be a key component with many challenges and opportunities ahead. In this study, different indazole- and benzotriazolebisphosphonic acids were prepared and incorporated into new Nafion-doped membranes up to a 5 wt% loading. The new membranes were characterised, and their proton conductivities were evaluated using electrochemical impedance spectroscopy. Membranes with a 1 wt% loading showed better proton conductivities than Nafion N-115 at all temperature and under relative humidity conditions studied. In these conditions, the best value was observed for the membrane doped with [hydroxy(1*H*-indazol-3-yl)methanediyl]bis(phosphonic acid) (BP2), with a proton conductivity of 98 mS cm^{-1}. Activation energy (E_a) values suggests that both Grotthuss and vehicular mechanisms are involved in the proton conduction across the membrane.

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1. Introduction

The worldwide demand for energy is still growing, resulting in the reduction of fossil fuel reserves and an increase in environmental problems. Cleaner, sustainable, renewable and environmentally friendly sources for energy systems are crucial challenges of the 21st century. Most countries have already established an increase in their energy production from renewable sources. Therefore, zero emission energy systems have attracted considerable attention and fostered increased efforts and investments. However, most renewable energy sources are low density and remain unstable and intermittent production sources.[1–4]

Among the cleaner energy technologies, fuel cells have become an alternative to the use of fossil fuel sources of energy. Fuel cells are electrochemical devices that convert the chemical energy stored in a fuel directly to electrical energy, with high efficiency and low environmental impact. Proton exchange membrane fuel cells (PEMFCs) are promising conversion devices amongst fuel cells due to their properties, including their high power-to-weight ratio and high power density.[5–18]

A drawback of the known PEM technology is the strong dependence of the proton conductivity on the water content of the membrane due to their operation under water-assisted proton conduction. This gives rise to several concerns regarding water and heat management, slow electrode reaction kinetics and water condensation, which consequently limit the operation of the membrane to temperatures up to the boiling point of water. At high temperatures, such drawbacks are surpassed, and PEMFCs can increase their performance and present high energy efficiency, but they can also show a lower thermal stability and the dehydration of the membrane with the loss of proton conductivity.[13–19] The membrane is regarded as a key material affected by its chemical and structural stability, its permeability to the fuel and the oxidant, as well as the humidity and temperature conditions, and consequently its proton conduction. Commercial membranes for PEMFCs are being made of organic polymers with acidic functionalities (including sulfonic, carboxylic and phosphonic acid groups), but their proton transport conduction still depends on the presence of conducting water or other electrolyte contents, which usually limit their operation to temperatures below 90 °C.[5–18]

The most studied and used PEMs are Nafion membranes, which have excellent chemical stability and high proton conductivity. This membrane is a hydrophobic perfluorosulfonated polymer with sulfonic acid groups capable of donating protons, whose transport is carried out through water molecule content, which limits its operation to 80 °C.[20–26] Most of the early studies were performed on membranes with sulfonic acid groups as proton carriers, but some studies showed that phosphonic acid can act as a better proton carrier since its proton transfer has a lower energy penalty (37.2 kJ mol^{-1}) than the sulfonic acid group (69.9 kJ mol^{-1}). Also, the phosphonic acid group can have both

[a] Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal. E-mail: carmen.rangel@lneg.pt
[b] Departamento de Química, ECT & Centro de Química de Évora, IIFA, Universidade de Évora, R. Romão Ramalho, 59, 7000-671 Évora, Portugal